DAS HERZ DER FRISCHE

REFRIGERANT REPORT 21

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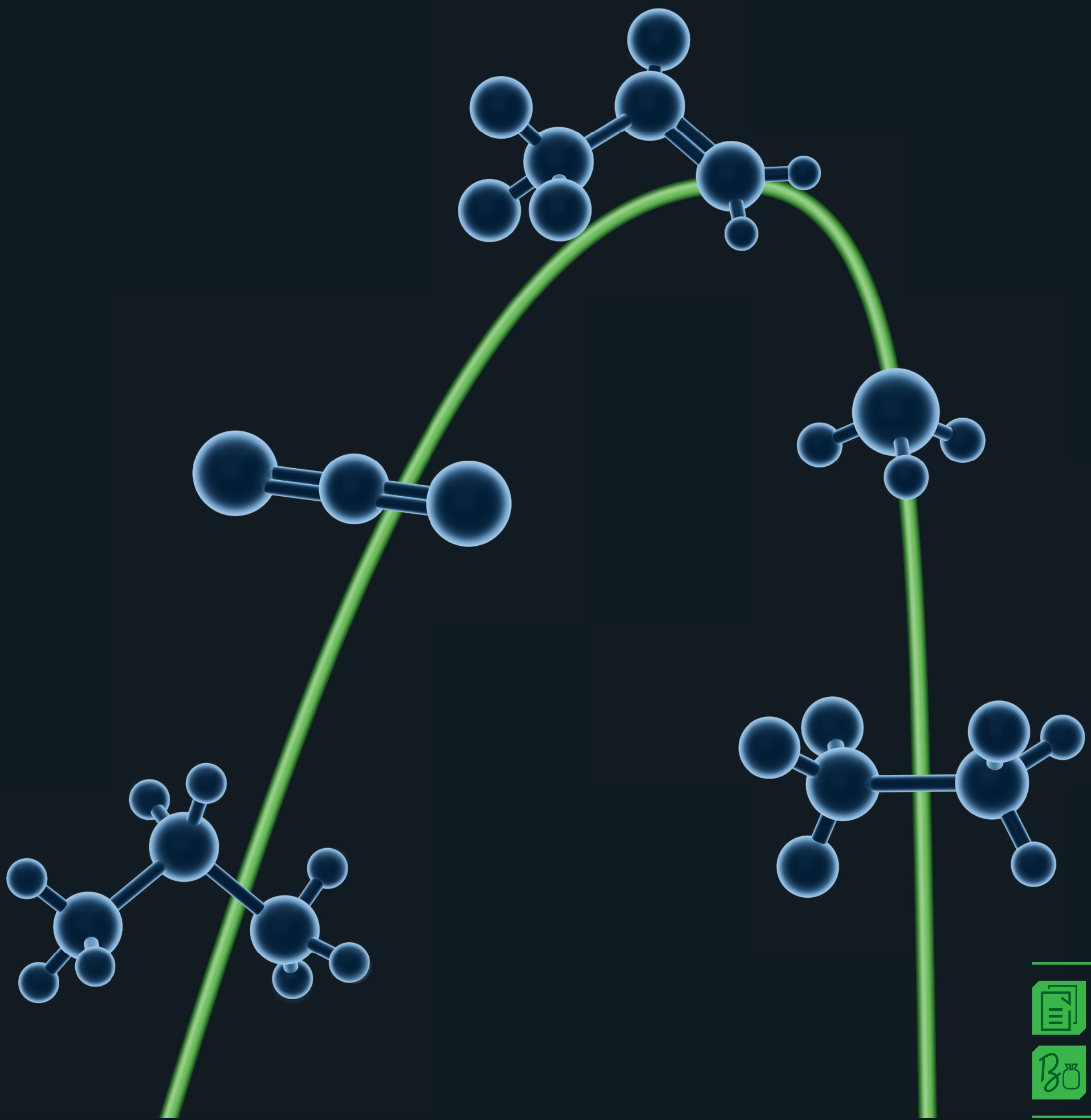

DOCUMENTATION

REFRIGERANT RULER APP

Contents **Page**

to the BITZER Refrigerant Ruler App

Android

iOS

to the digital Refrigerant Report

This edition supersedes all previous issues.

Stratospheric ozone depletion as well as atmospheric greenhouse effect due to refrigerant emissions have led to drastic changes in the refrigeration and air conditioning technology since the beginning of the 1990s.

This is especially true for the area of commercial refrigeration and air conditioning systems with their wide range of applications. In former years the main refrigerants used for these systems were ozone depleting types, namely R12, R22 and R502; for special applications R114, R12B1, R13B1, R13 and R503 were used.

The use of these substances is no longer allowed in industrialised countries, but the use of R22 has been extended through transitional periods. However, the European Union also commited to an early phase-out for R22, which was enforced in several stages (see page 8). The main reason for this early ban of R22 contrary to the international agreement is the ozone depletion potential although it is only small.
Since 2010, phase-out regulations became effective in other countries as well, for instance in the USA.

This implies enormous consequences for the whole refrigeration and air conditioning sector. BITZER therefore committed itself to taking a leading role in the research and development of environmentally friendly system designs.

After the chlorine-free (ODP = 0) HFC refrigerants R134a, R404A, R407C, R507A and R410A have become widely established for many years in commercial refrigeration, air conditioning and heat pump systems, new challenges have come up. They concern primarily the greenhouse effect: The aim is a clear reduction of direct emissions caused by refrigerant losses and indirect emissions by particularly efficient system technology.

In this area, applicable legal regulations are already in force, such as the EU F-Gas Regulation No. 517/2014 (BITZER brochure A-510) and a series of regulations already ratified or in preparation as part of the EU Ecodesign Directive (BITZER brochure A-530). Similar regulations are also in preparation or already implemented in Australia, Canada and the USA. On an international level, the so-called "Kigali Amendment" was adopted in 2016 under the Montreal Protocol, in which a step-by-step reduction of HFCs ("HFC phase-down") was agreed upon starting in 2019.
Even though indirect emissions caused by energy production are considerably higher than direct (CO_2-equivalent) emissions caused by HFC refrigerants, refrigerants with high global warming potential (GWP) will in the future be subject to use restrictions or bans. This will affect primarily R404A and R507A, for which alternatives with lower GWP are already being offered. However, in order to achieve the legal objectives, substitutes for further refrigerants and increased use of naturally occurring substances (NH_3, CO_2, hydrocarbons) will become necessary.

This requires comprehensive testing of these refrigerants, suitable oils and adjusted systems. Therefore a close co-operation exists with scientific institutions, the refrigeration and oil industries, component manufacturers as well as a number of innovative refrigeration and air conditioning companies.

A large number of development tasks have been completed. Suitable compressors for alternative refrigerants are available.

Besides the development projects, BITZER actively supports legal regulations and self commitments concerning the responsible use of refrigerants as well as measures to increase system and components' efficiency.

The following report deals with potential measures of a short to medium-term change towards technologies with reduced environmental impact in medium and large size commercial and industrial refrigeration, air conditioning and heat pump systems. Furthermore, the experiences so far and the resulting consequences for plant technology are discussed.

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Several studies confirm that vapour compression refrigeration systems normally used commercially are far superior in efficiency to all other processes down to a cold space temperature of around -40°C.

The selection of an alternative refrigerant and the system design receives special significance, however. Besides the request for substances without ozone depletion potential (ODP = 0) especially the energy demand of a system is seen as an essential criterion due to its indirect contribution to the greenhouse effect. On top of that there is the direct global warming potential (GWP) due to refrigerant emission.

Therefore a calculation method has been developed for the qualified evaluation of a system which enables an analysis of the total influence on the greenhouse effect. The so-called "TEWI" factor (**T**otal **E**quivalent **W**arming **I**mpact) has been introduced. Meanwhile, another, more extensive assessment method has been developed considering "Eco-Efficiency". Hereby, both ecological (such as TEWI) and economical criteria are taken into account (further explanations see page 7).

Therefore it is possible that the assessment of refrigerants with regard to the environment can differ according to the place of installation and drive method.

Upon closer evaluation of substitutes for the originally used CFC and HCFC as well as for HFCs with higher GWP, the options with single-substance refrigerants are very limited. This includes e.g. R134a, which will be usable for quite some time based on its comparatively low GWP. Similarly, the hydro-fluoro-olefins (HFO) R1234yf and R1234ze(E) with a GWP < 10, which are also exempted from the F-Gas regulation.

Direct alternatives (based on fluorinated hydrocarbons) for almost all refrigerants of higher volumetric refrigerating capacity and pressure level than R134a can (mainly) only be "formulated" as blends. However, taking into account thermodynamic properties, flammability, toxicity and global warming potential, the list of potential candidates is very limited. Blends of reduced GWP include in addition to R134a, R1234yf and R1234ze(E) primarily the refrigerants R32, R125 and R152a.

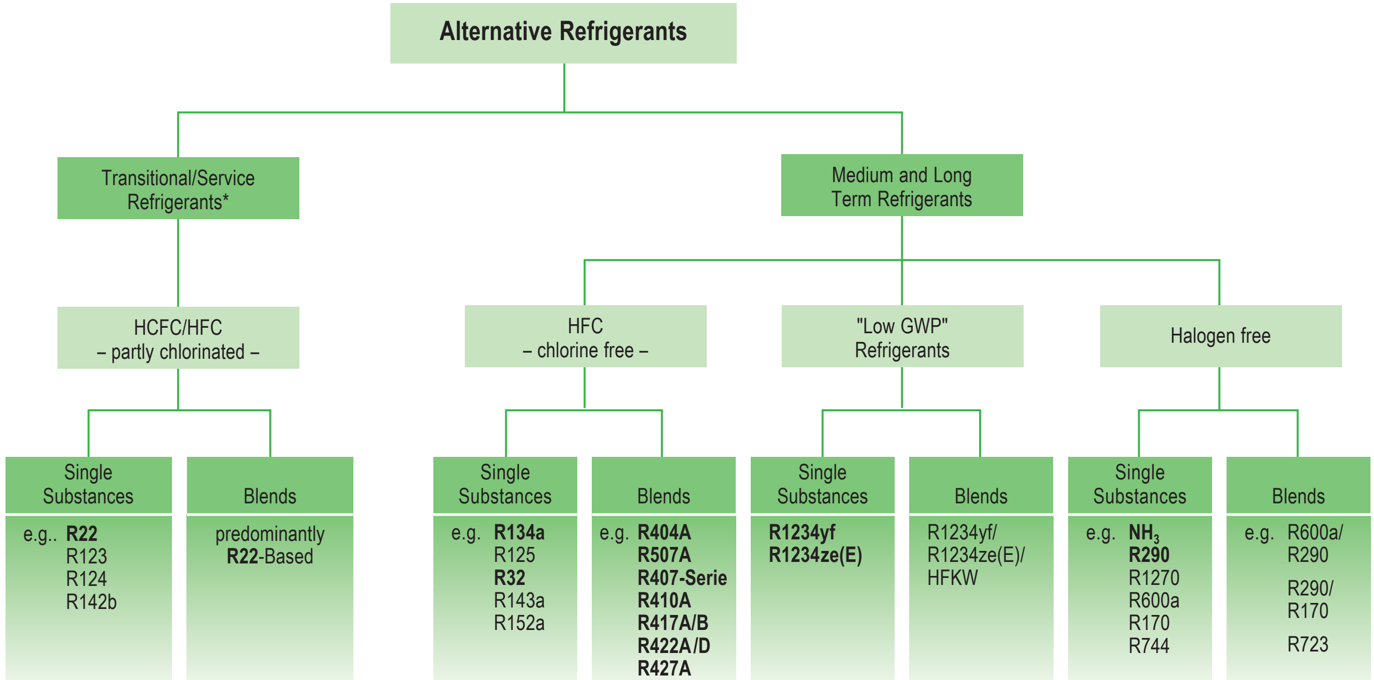
Besides halogenated refrigerants, Ammonia (NH_3) and hydrocarbons are considered as substitutes as well. The use for commercial applications, however, is limited by strict safety requirements.

Carbon dioxide (CO_2) becomes more important as an alternative refrigerant and secondary fluid, too. Due to its specific characteristics, however, there are restrictions to a general application.

The following illustrations show a structural survey of the alternative refrigerants and a summary of the single or blended substances which are now available. After that the individual subjects are discussed.

For refrigerant properties, application ranges and lubricant specifications, see pages 42 to 45.

For reasons of clarity the less or only regionally known products are not specified in this issue, which is not intended to imply any inferiority.



* Service refrigerants contain HCFC as blend component. They are therefore subject to the same legal regulations as R22 (see page 8).
As a result of the continued refurbishment of older installations, the importance of these refrigerants is clearly on the decline. For some of them, production has already been discontinued. However, because of the development history of service blends, these refrigerants will continue to be covered in this Report.

Fig. 1 Structural classification of refrigerants

HFC refrigerants

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Former Refrigerants	Alternatives				
	ASHRAE Classification	**Trade name**		**Composition (with blends)**	**Detailed Information**
R12 (R500)	**R134a** **R152a** ① **R437A** ④	– – ISCEON® MO49 Plus	 Chemours	– – R125/134a/600/601	pages 9...12, 16, 42...44
R22/R502	**R404A** **R507A** **R422A**	various various ISCEON® MO79	 Chemours	R143a/125/134a R143a/125 R125/134a/600a	pages 17...19, 42...44
R22	**R407A** **R407C** **R407F** **R407H** **R410A** **R417A** **R417B** **R422D** **R427A** **R438A**	– various Performax® LT – various ISCEON® MO59 – ISCEON® MO29 Forane® 427A ISCEON® MO99	Koura (Mexichem), Arkema Honeywell Daikin Chemical Chemours Daikin Chemical Chemours Arkema Chemours	R32/125/134a R32/125/134a R32/125/134a R32/125/134a R32/125 R125/134a/600 R125/134a/600 R125/134a/600a R32/125/143a/134a R32/125/134a/600/601a	pages 18...23, 42...44
R114 R12B1	**R236fa** **R227ea**	– –		– –	pages 37, 41...43
R13B1	**R410A**	various		R32/125	pages 39, 42...44
R13 R503	**R23** **R508A** **R508B**	– KLEA® 508A Suva® 95	 Koura (Mexichem) Chemours	– R23/116 R23/116	pages 40, 42...44

Tab. 1 Substitutes for CFC and HCFC refrigerants (chlorine free HFCs)

HFO and HFO/HFC Blends

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Current Refrigerants	Alternatives				
	ASHRAE Classification	Trade name		Composition (with blends)	Detailed Information
R134a	R1234yf ①	various		–	pages 24…27, 42…44
	R1234ze(E) ①	various		–	
	R450A	Solstice® N-13	Honeywell	R1234ze(E)/134a	
	R456A	AC5X	Koura (Mexichem)	R32/1234ze(E)/134a	
	R513A	Opteon™ XP10 R513A	Chemours Daikin Chemical	R1234yf/134a	
	R516A	ARM-42	Arkema	R1234yf/152a/134a	
R404A/R507A* (R22/R407C*)	R448A	Solstice® N-40	Honeywell	R32/125/1234yf/1234ze(E)/134a	pages 24…27, 42…44
	R449A	Opteon™ XP40 Forane® 449	Chemours Arkema	R32/125/1234yf/134a	
	R449C	Opteon™ XP20	Chemours	R32/125/1234yf/134a	
R410A	R32 ①	various		–	pages 24…27, 42…44
	R452B ①	Opteon™ XL55 Solstice® L-41y	Chemours Honeywell	R32/125/1234yf	
	R454B ①	Opteon™ XL41	Chemours	R32/1234yf	

* Due to the large number of different HFO/HFC blends and the potential changes in development products, the above list contains as alternatives for R134a and R404A/R507A only non-flammable blends of GWP approx. 600 (R134a) and GWP < 1500 (R404A/R507A).
For an extensive discussion of HFO/HFC blends: see chapter "Low GWP" HFOs and HFO/HFC blends as alternatives to HFCs, page 24.
Further alternatives are also dealt with.

Tab. 2 "Low GWP" refrigerants and blends

Halogen free refrigerants

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Current Refrigerants	Alternatives			
	ASHRAE Classification	Trade name	Formula	Detailed Information
R134a	R290/600a ① R600a ① ③	– –	C_3H_8/C_4H_{10} C_4H_{10}	pages 30, 42...44
R404A R507A R22	R717 ① ② R723 ① ② R290 ① R1270 ①	– – – –	NH_3 NH_3 + R-E170 C_3H_8 C_3H_6	pages 28...32, 42...44
R124	R600a ①	–	C_4H_{10}	pages 37, 42...44
R410A	no direct alternatives available			
R23	R170 ①	–	C_2H_6	pages 39, 42...44
Various	R744 ③	–	CO_2	pages 33...36, 42...44

Tab. 3 Alternatives for HCFC and HFC refrigerants (halogen free refrigerants)

Explanation of Tab. 1 to 3 ① Flammable ② Toxic ③ Large deviation in refrigerating capacity and pressures to the previous refrigerant ④ Service refrigerant with zero ODP

Global Warming and TEWI Factor

As already mentioned (see chapter Refrigerant developments and legal situation, page 3), a method of calculation has been developed to judge the influence upon the global warming effect for the operation of individual refrigeration plants (TEWI = **T**otal **E**quivalent **W**arming **I**mpact).

All halocarbon refrigerants (including the non-chlorinated HFCs) belong to the category of greenhouse gases. An emission of these substances contributes to the global warming effect. The influence is however much greater in comparison to CO_2, which is the main greenhouse gas in the atmosphere (in addition to water vapour). Based on a time horizon of 100 years, the emission from 1 kg R134a is for example roughly equivalent to 1430 kg of CO_2 (GWP = 1430).

Thus, the reduction of refrigerant losses must be one of the main tasks for the future.

On the other hand, the major contributor to a refrigeration plant's global warming effect is the (indirect) CO_2 emission caused by energy generation. Based on the high percentage of fossil fuels used in power stations, the average European CO_2 release is around 0.365 kg per kWh* of electrical energy. This results in a significant greenhouse effect over the lifetime of the plant.

Due to a deciding proportion of the total balance, there is not only a need for alternative refrigerants with a favorable (thermodynamic) energy balance, but an increase in demand for **highly efficient compressors** and associated equipment as well as optimised system components and system control.

When various compressor designs are compared, the difference of indirect CO_2 emission (due to the energy requirement) can have a larger influence upon the total effect than the refrigerant losses.

A usual formula is shown in Fig. 2. The TEWI factor can be calculated and the various areas of influence are correspondingly separated.

Additionally, the following figure (Fig. 3) shows TEWI values with various refrigerant charges, leakage losses and energy consumptions (example: medium temperature with R134a).

This example is simplified based on an overall leak rate as a percentage of the refrigerant charge. The actual values vary very strongly, so that the potential risk of individually constructed systems and extensively branched plants is especially high.

Great effort is taken worldwide to reduce greenhouse gas emissions, and legal regulations have partly been developed already. Since 2007, the "Regulation on certain fluorinated greenhouse gases" – which also defines stringent requirements for refrigeration and air conditioning systems – has become valid for the EU. Meanwhile, the revised Regulation No. 517/2014 entered into force and has to be applied since January 2015.

TEWI = **T**OTAL **E**QUIVALENT **W**ARMING **I**MPACT

$$TEWI = (GWP \times L \times n \ + (GWP \times m \,[\, 1 - \alpha_{recovery}]) \ + (n \times E_{annual} \times \beta)$$

Leakage	Recovery losses	Energy consumption
direct global warming potential		indirect global warming potential

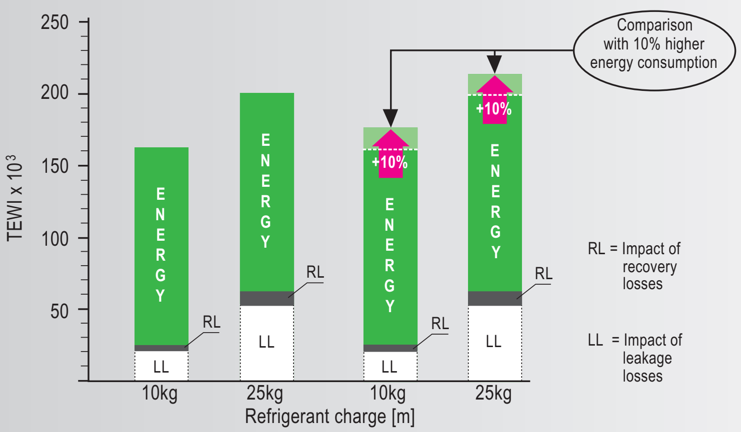
GWP	= Global warming potential	[CO_2-related acc. to IPCC IV]
L	= Leakage rate per year	[kg]
n	= System operating time	[Years]
m	= Refrigerant charge	[kg]
$\alpha_{recovery}$	= Recycling factor	
E_{annual}	= Energy consumption per year	[kWh]
β	= CO_2-Emission per kWh	(Energy-Mix)

Fig. 2 Method for the calculation of TEWI figures

Example

Medium temperature R134a

SST	-10 °C
SCT	+40 °C
m	10 kg // 25 kg
$L_{[10\%]}$	1 kg // 2.5 kg
CAP	13.5 kW
E	5 kW x 5000 h/a
β	0.365 kg CO_2/kWh*
α	0.75
η	15 years
GWP	1430 (CO_2 = 1)
	time horizon 100 years



* Average for EU 2019, source: www.carbonfootprint.com

Fig. 3 Comparison of TEWI figures (example)

Eco-Efficiency

An assessment based on the specific TEWI value takes into account the effects of global warming during the operating period of a refrigeration, air conditioning or heat pump installation. However, not the entire ecological and economical aspects are considered.

But apart from ecological aspects, economical aspects are highly significant when evaluating technologies and making investment decisions. With technical systems, the reduction of environmental impact frequently involves high costs, whereas low costs often have increased ecological consequences. For most companies, the investment costs are decisive, whereas they are often neglected during discussions about minimizing ecological problems.

For the purpose of a more objective assessment, studies* were presented in 2005 and 2010, using the example of supermarket refrigeration plants to describe a concept for evaluating **Eco-Efficiency**. It is based on the relationship between added value (a product's economic value) and the resulting environmental impact.

With this evaluation approach, the entire life cycle of a system is taken into account in terms of:

- ❑ ecological performance in accordance with the concept of Life Cycle Assessment as per ISO 14040,
- ❑ economic performance by means of a Life Cycle Cost Analysis.

This means that the overall environmental impact (including direct and indirect emissions), as well as the investment costs, operating and disposal costs, and capital costs are taken into account.

The studies also confirm that an increase of Eco-Efficiency can be achieved by investing in optimized plant equipment (minimized operating costs). Hereby, the choice of refrigerant and the associated system technology play an important role.

Eco-Efficiency can be illustrated in graphic representation (example, see Fig. 5). The results of the Eco-Efficiency evaluation are shown on the x-axis in the system of coordinates, whilst the results of the life cycle cost analysis are shown on the y-axis. This shows clearly: A system that is situated higher in the top right quadrant exhibits an increasingly better Eco-Efficiency – and conversely, it becomes less efficient in the bottom left sector.

The diagonals plotted into the system of coordinates represent lines of equal Eco-Efficiency. This means that systems or processes with different life cycle costs and environmental impacts can quite possibly result in the same Eco-Efficiency.

* Study 2005: Compiled by Solvay Management Support GmbH and Solvay Fluor GmbH, Hannover, together with the Information Centre on Heat Pumps and Refrigeration (IZW), Hannover.

Study 2010: Compiled by SKM ENVIROS, UK, commissioned by and in cooperation with EPEE (European Partnership for Energy and Environment).

Both projects were supported by an advisory group of experts from the refrigeration industry.

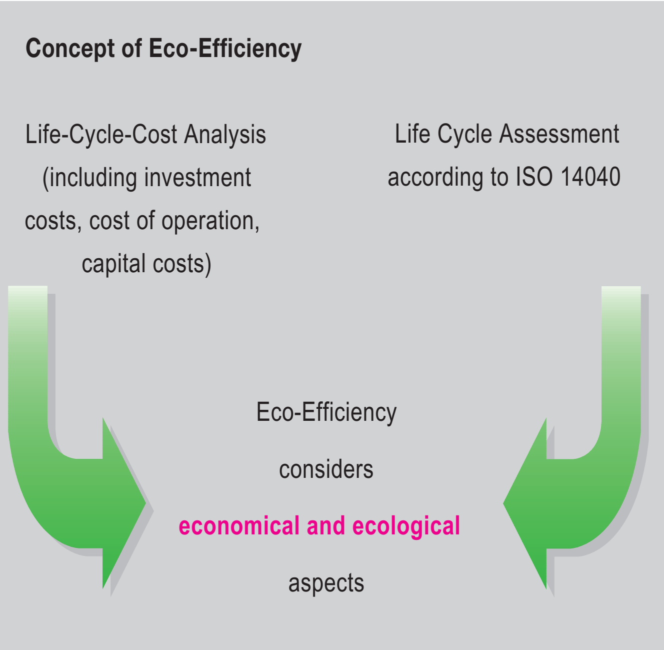


Fig. 4 Concept of Eco-Efficiency

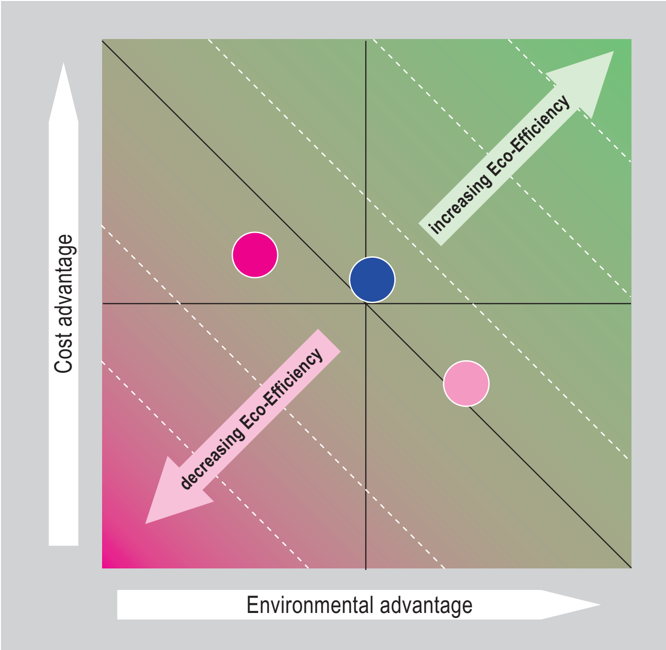


Fig. 5 Example of an Eco-Efficiency evaluation

R22 as transitional refrigerant

Although chlorine-free refrigerants, such as R134a and R404A/R507A (Fig. 1 and Tab. 1) have been widely used − but are already being replaced by alternatives with lower GWP in the EU for example − R22 is still used internationally in many areas, both for new installations and for retrofitting existing ones.

Reasons are relatively low investment costs, especially compared with R134a systems, but also its large application range, favourable thermodynamic properties and low energy requirement. Additionally, R22 and components are still widely available, which is not guaranteed everywhere for the alternatives.

Despite of the generally favourable properties R22 is already subject to various regional restrictions* which control the use of this refrigerant in new systems and for service purposes due to its ozone depletion potential – although being low.

With regard to components and system technology a number of particularities are to follow as well. Refrigerant R22 has approximately 55% higher refrigerating capacity and pressure levels than R12**. The significantly higher discharge gas temperature is also a critical factor compared to R12 (Fig. 6) and R502**.

Similar relationships in terms of thermal load are found in the comparison with HFC refrigerants R134a, R404A/R507A (pages 9 and 17).

Resulting design criteria

Particularly critical – due to the high discharge gas temperature – are low temperature plants especially concerning thermal stability of oil and refrigerant, with the danger of acid formation and copper plating.

Special measures have to be adopted therefore, such as two stage compression, controlled refrigerant injection, additional cooling, monitoring of discharge gas temperature, limiting the suction gas superheat and particularly careful installation.

* Not allowed for new equipment in Germany and Denmark since January 1st, 2000 and in Sweden as of 1998.

Since January 1st, 2001 restrictions apply to the other member states of the EU as well. The measures concerned are defined in the ODS Regulation 1005/2009 of the EU commision on ozone depleting substances amended in 2009. This regulation also governs the use of R22 for service reasons within the entire EU.

Since 2010, phase-out regulations in other countries, such as the USA, are valid.

** Already banned in most countries.

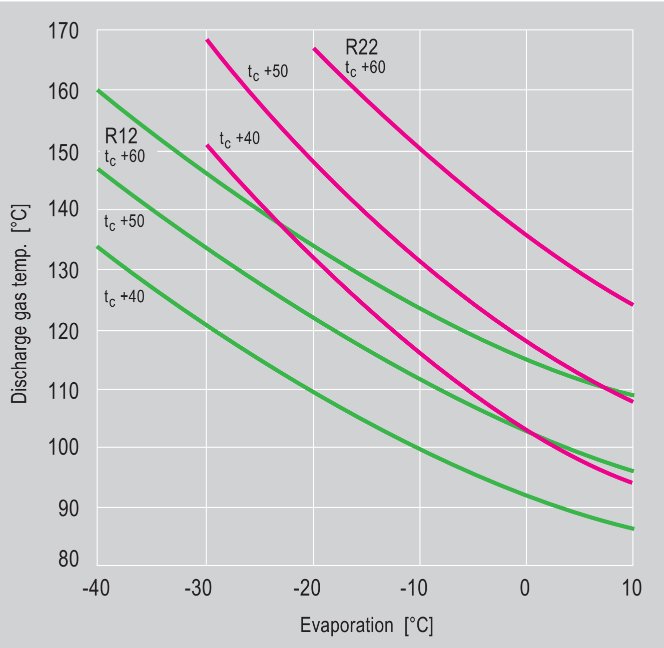


Fig. 6 R12/R22 – comparison of discharge gas temperatures of a semi-hermetic compressor

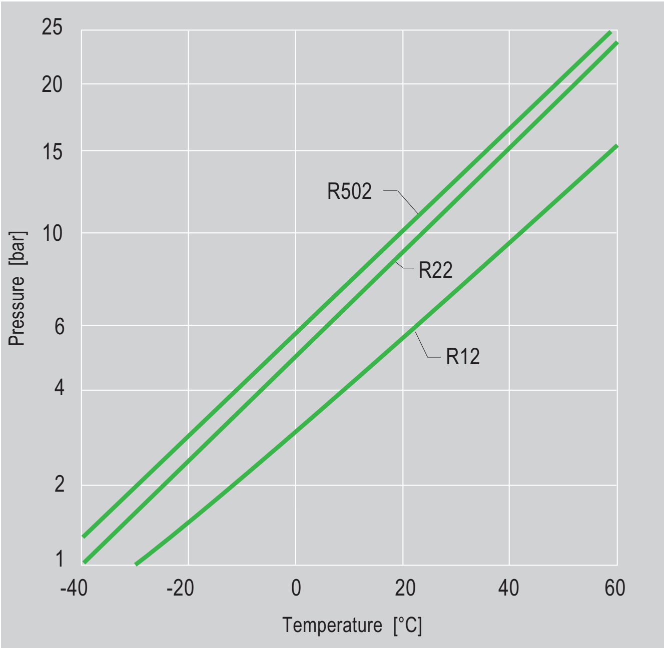


Fig. 7 R12/R22/R502 – comparison of pressure levels

R134a as substitute for R12 and R22

R134a was the first chlorine free (ODP = 0) HFC refrigerant that was tested comprehensively. It is now used world-wide in many refrigeration and air conditioning units with good results. As well as being used as a pure substance, R134a is also applied as a component of a variety of blends.

R134a has similar thermodynamic properties to R12:

Refrigerating capacity, energy demand, temperature properties and pressure levels are comparable, at least in air conditioning and medium temperature refrigeration plants. This refrigerant can therefore be used as an alternative for most former R12 applications.

For some applications **R134a is even preferred as a substitute for R22**, an important reason being the limitations to the use of R22 in new plants and for service. However, the lower volumetric refrigerating capacity of R134a (Fig. 9) requires a larger compressor displacement than with R22.

There are also limitations in the application with low evaporating temperatures to be considered.
Comprehensive tests have demonstrated that the performance of R134a exceeds theoretical predictions over a wide range of compressor operating conditions. Temperature levels (discharge gas, oil) are even lower than with R12 and, therefore, substantially lower than R22 values. There are thus many potential applications in air conditioning and medium temperature refrigeration plants as well as in heat pumps. Good heat transfer characteristics in evaporators and condensers (unlike zeotropic blends) favour an economical use.

R134a is also characterized by a comparably low GWP (1430). Therefore, in view of future restrictions (for example EU F-Gas Regulation), the use of this refrigerant will still be possible for quite some time. If required, systems can later be converted relatively easily to non-flammable (A1) HFO/HFC alternatives with a GWP of approx. 600 (Tab. 5).

Lubricants for R134a and other HFCs

The traditional mineral and synthetic oils are not miscible (soluble) with R134a and other HFCs described in the following and are therefore only insufficiently transported around the refrigeration circuit.

Immiscible oil can settle out in the heat exchangers and prevent heat transfer to such an extent that the plant can no longer be operated.

New lubricants were developed with the appropriate solubility and have been in use for many years. These lubricants are based on Polyol Ester (POE) and Polyalkylene Glycol (PAG).

For further explanations on lubricants see chapter "Lubricants for compressors", page 41.

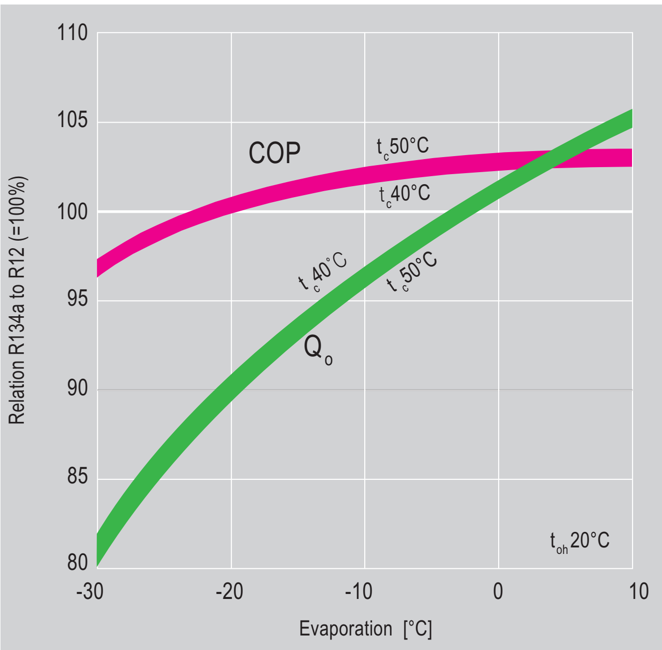


Fig. 8 R134a/R12 – comparison of performance data of a semi-hermetic compressor

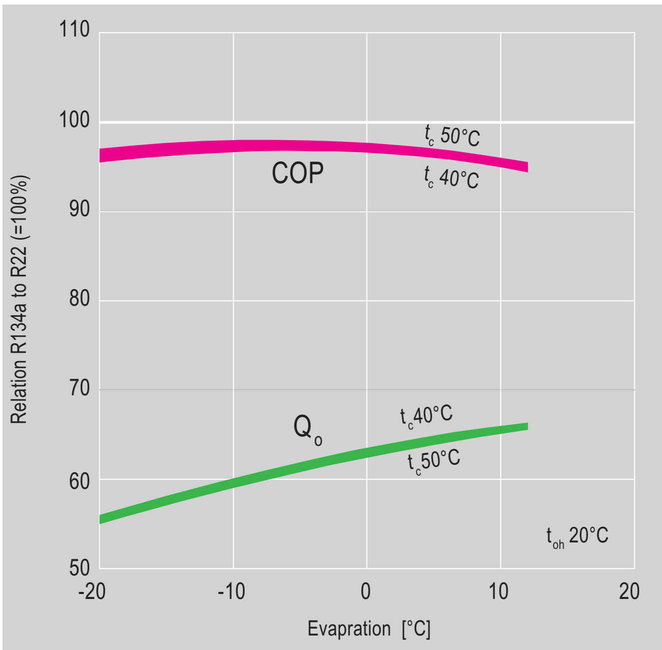


Fig. 9 R134a/R22 – comparison of performance data of a semi-hermetic compressor

Resulting design and construction criteria

Suitable compressors are required for R134a with a special oil charge and adapted system components. The normal metallic materials used in CFC plants have also been proven with ester oils; elastomers must sometimes be matched to the changing situation. This is especially valid for flexible hoses where the requirements call for a minimum residual moisture content and low permeability.

The plants must be dehydrated with particular care and the charging or changing of lubricant must also be done carefully. In addition relatively large driers should be provided, which have also to be matched to the smaller molecule size of R134a.

Meanwhile, many years of very positive experience with R134a and ester oils have been accumulated. For this refrigerant, BITZER offers an unequalled wide range of reciprocating, screw and scroll compressors.

Converting existing R12 plants to R134a

At the beginning this subject was discussed very controversially, several conversion methods were recommended and applied. Today there is a general agreement on technically and economically matching solutions.
The characteristics of ester oils are very favourable here: Under certain conditions they can be used with CFC refrigerants, they can be mixed with mineral oils and tolerate a proportion of chlorine up to a few hundred ppm in an R134a system.

The remaining moisture content has, however, an enormous influence. Very thorough evacuation (removal of remaining chlorine and dehydration) is therfore essential, as well as the installation of generously dimensioned driers. There is doubtful experience with systems where the chemical stability was already insufficient with R12 operation e.g. with bad maintenance, small drier capacity, high thermal loading. Increased deposition of oil decomposition products containing chlorine is found often. These products are released by the influence of the highly polarized mixture of ester oil and R134a and find their way into the compressor and control devices. Conversion should therefore be limited to systems which are in a good condition.

Restrictions for R134a in mobile air conditioning (MAC) systems

An EU Directive on "Emissions from MAC systems" bans the use of R134a in new systems. Various alternative technologies are already in use. For further explanations see pages 11 and 36).

Supplementary BITZER information concerning the use of R134a (see also https://www.bitzer.de)

- **Technical Information KT-500 „BITZER refrigeration compressor oils for reciprocating compressors“**

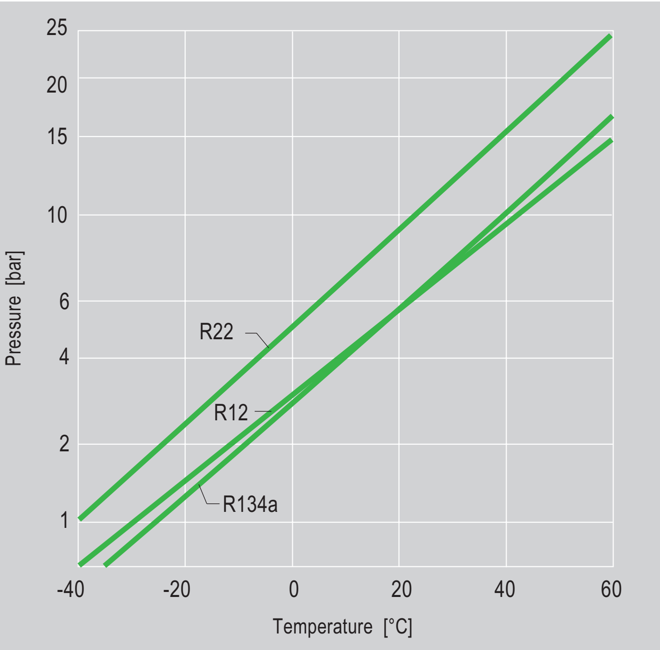


Fig. 10 R134a/R12/R22 – comparison of pressure levels

Alternatives to R134a

For mobile air conditioning systems (MAC) with open drive compressors and hose connections in the refrigerant circuit, the risk of leakages is considerably higher than with stationary systems. An EU Directive (2006/40/EC) has been passed to reduce direct emissions in this application area. Within the scope of the Directive, and starting 2011, type approvals for new vehicles will only be granted if they use refrigerants with a global warming potential (GWP) of less than 150. Consequently, this excludes R134a (GWP = 1430) which has been used so far in these systems.

Meanwhile, alternative refrigerants and new technologies were developed and tested. This also involved a closer examination of the use of R152a.

For quite some time the automotive industry has agreed on so-called "Low GWP" refrigerants. The latter is dealt with as follows.

CO_2 technology, favored for this application for quite some time, has not been widely implemented for a variety of reasons (pages 12 and 36).

R152a – an alternative to R134a (?)

R152a is very similar to R134a with regard to volumetric refrigerating capacity (approx. -5%), pressure levels (approx. -10%) and energy efficiency. Mass flow, vapour density and thus also the pressure drop are even more favourable (approx. -40%).

R152a has been used for many years as a component in blends, but not as a single substance refrigerant till now. Especially advantageous is the very low global warming potential (GWP = 124).

R152a is flammable – due to its low fluorine content – and classified in safety group A2. As a result, increased safety requirements demand individual design solutions and safety measures along with the corresponding risk analysis.

For this reason, the use of R152a in mobile air conditioning systems for passenger cars (MAC) has not been implemented yet.

"Low GWP" HFO refrigerant R1234yf

The ban on the use of R134a in mobile air conditioning systems within the EU has triggered a series of research projects. In addition to CO_2 technology (see chapter CO_2 in mobile air conditioning systems, page 36), refrigerants with very low GWP values and similar thermodynamic properties as R134a have been developed.

In early 2006, two refrigerant mixtures were introduced under the names "Blend H" (Honeywell) and "DP-1" (DuPont). INEOS Fluor followed with another version under the trade name AC-1. In the broadest sense, all of these refrigerants were blends of various fluorinated molecules.

During the development and test phase it became obvious that not all acceptance criteria could be met, and thus further examinations with these blends were discontinued.
Consequently, DuPont (meanwhile Chemours) and Honeywell bundled their research and development activities in a joint venture which focused on 2,3,3,3-tetrafluoropropene ($CF_3CF{=}CH_2$). This refrigerant, designated R1234yf, belongs to the group of hydro fluoro olefins (HFO). These refrigerants are unsaturated HFCs with a chemical double bond.

The global warming potential is extremely low (GWP = 4). When released to the atmosphere, the molecule rapidly disintegrates within a few days, resulting in a very low GWP. This raises certain concerns regarding the long-term stability in refrigeration circuits under real conditions.
However, extensive testing has demonstrated the required stability for mobile air conditioning systems.

R1234yf has lower flammability as measured by ASTM 681, but requires significantly more ignition energy than R152a, for instance. Due to its low burning velocity and the high ignition force, it received a classification of the new safety group "A2L" according to ISO 817.

In extensive test series, it has been shown that a potentially increased risk of the refrigerant flammability in MAC systems can be avoided by implementing suitable constructive measures. However, some investigations (e.g. by Daimler) also show an increased risk. This is why various manufacturers have intensified again the development of alternative technologies.

Toxicity investigations have shown very positive results, as well as compatibility tests of the plastic and elastomer materials used in the refrigeration circuit. Some lubricants show increased chemical reactivity which, however, can be suppressed by a suitable formulation and/or addition of "stabilizers".

Operating experiences gained from laboratory and field trials to date allow a positive assessment, particularly with regard to performance and efficiency behaviour. For the usual range of mobile air conditioning operation, refrigerating capacity and coefficient of performance (COP) are within a range of 5% compared with that of R134a. Therefore, it is expected that simple system modifications will provide the same performance and efficiency as with R134a.

The critical temperature and pressure levels are also similar, while the vapour densities and mass flows are approximately 20% higher. The discharge gas temperature with this application is up to 10 K lower.

With a view to the relatively simple conversion of mobile air conditioning systems, this technology prevailed up to now over the competing CO_2 systems.

However, as already explained before, due to the flammability of R1234yf, investigations focus on other technical solutions. This includes active fire-extinguishing devices (e.g. with argon), but also enhancements of CO_2 systems.

For detailed information on properties and the application, see chapter "Low GWP" HFOs and HFO/HFC blends as alternatives to HFCs, page 24.

Refrigerant blends

Refrigerant blends have been developed for existing as well as for new plants with properties making them comparable alternatives to the previously used substances.

It is necessary to distinguish between three categories:

1. **Transitional or service blends**
   which mostly contain HCFC R22 as the main constituent. They are primarily intended as **service refrigerants for older plants** with view on the use ban of R12, R502 and other CFCs. Corresponding products are offered by various manufacturers, there is practical experience covering the necessary steps of conversion procedure.

   However, the same legal requirements as for R22 apply to the use and phase-out of these blends (see page 8).

2. **HFC blends**
   These are substitutes for the refrigerants R502, R22, R13B1 and R503. Above all, R404A, R507A, R407C and R410A, are being used to a great extent.
   One group of these HFC blends also contains hydrocarbon additives. The latter exhibit an improved solubility with lubricants, and under certain conditions they allow the use of conventional oils. In many cases, this permits the conversion of existing (H)CFC plants to chlorine-free refrigerants (ODP = 0) without the need for an oil change.

3. **HFO/HFC blends**
   as successor generation of HFC refrigerants. It concerns blends of new "Low GWP" refrigerants (e.g. R1234yf) with HFCs. The fundamental target is an additional decrease of the global warming potential (GWP) as compared to established halogenated substances (see page 24).

Blends of two and three components already have a long history in the refrigeration trade. A difference is made between the so called "azeotropes" (e.g. R502, R507A) with thermodynamic properties similar to single substance refrigerants, and "zeotropes" with "gliding" phase changes (also see next chapter). The original development of "zeotropes" mainly concentrated on special applications in low temperature and heat pump systems. Actual system construction, however, remained the exception.

A somewhat more common earlier practice was the mixing of R12 to R22 in order to improve the oil return and to reduce the discharge gas temperature with higher pressure ratios. It was also usual to add R22 to R12 systems for improved performance, or to add hydrocarbons in the extra low temperature range for a better oil transport.

This possibility of specific "formulation" of certain characteristics was indeed the basis for the development of a new generation of blends.

At the beginning of this Report (see chapter Refrigerant developments and legal situation, page 3) it was already explained that no direct single-substance alternatives (on the basis of fluorinated hydrocarbons) exist for the previously used and current refrigerants of higher volumetric refrigeration capacity than R134a. This is why they can only be "formulated" as blends. However, taking into account thermodynamic properties, flammability, toxicity and global warming potential, the list of potential candidates is strongly limited.

For the previously developed CFC and HCFC substitutes, the range of substances was still comparably large, due to the fact that substances of high GWP could also be used. However, for formulating blends with significantly reduced GWP, in addition to R134a, R1234yf and R1234ze(E), primarily refrigerants R32, R125 and R152a can be used. Most of them are flammable. They also exhibit considerable differences with respect to their boiling points, which is why all "Low GWP" blends of high volumetric refrigerating capacity have a substantial temperature glide (see next chapter).

BITZER has accumulated extensive experience with refrigerant blends. Laboratory and field testing was commenced at an early stage so that basic information was obtained for the optimizing of the mixing proportions and for testing suitable lubricants. Based on this data, a large supermarket plant – with 4 BITZER semi-hermetics in parallel – could already be commissioned in 1991. The use of these blends in the most varied systems has been state-of-the-art for many years – generally with good experiences.

General characteristics of zeotropic blends

As opposed to azeotropic blends (e.g. R502, R507A), which behave as single substance refrigerants with regard to evaporation and condensing processes, the phase change with zeotropic fluids occurs in a "gliding" form over a certain range of temperature.

This "temperature glide" can be more or less pronounced, it depends mainly on the boiling points and the percentage proportions of the individual components. Certain supplementary definitions are also used, depending on the effective values, such as "near-azeotrope" or "semiazeotrope" for less than 1 K glide.

Essentially, this results in a small temperature increase already in the evaporation phase and a reduction during condensing. In other words: At a certain pressure level, the resulting saturation temperatures differ in the liquid and vapour phases (Fig. 11).

To enable a comparison with single substance refrigerants, the evaporating and condensing temperatures have been often defined as mean values. As a consequence the measured subcooling and superheating conditions (based on mean values) are unrealistic. The effective difference – based on dew and bubble temperature – is less in each case. These factors are very important when assessing the minimum superheat at the compressor inlet (usually 5 to 7 K) and the quality of the refrigerant after the liquid receiver (vapour bubbles).

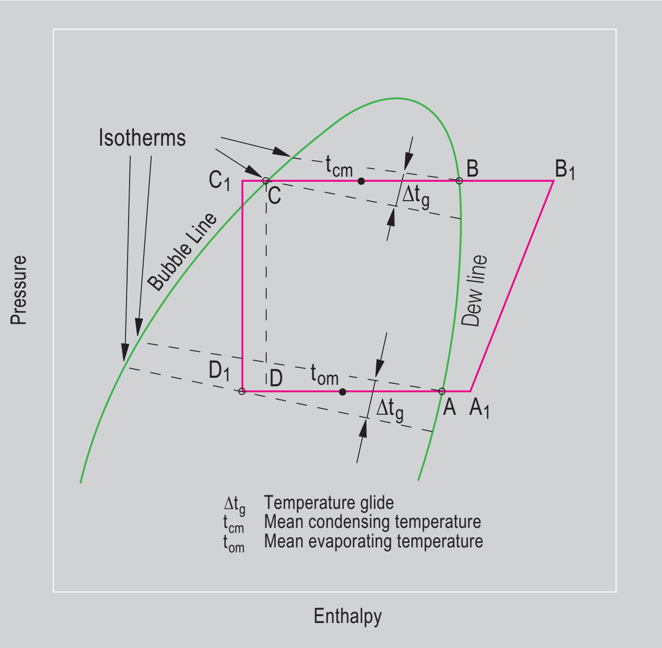


Fig. 11 Evaporating and condensing behavior of zeotropic blends

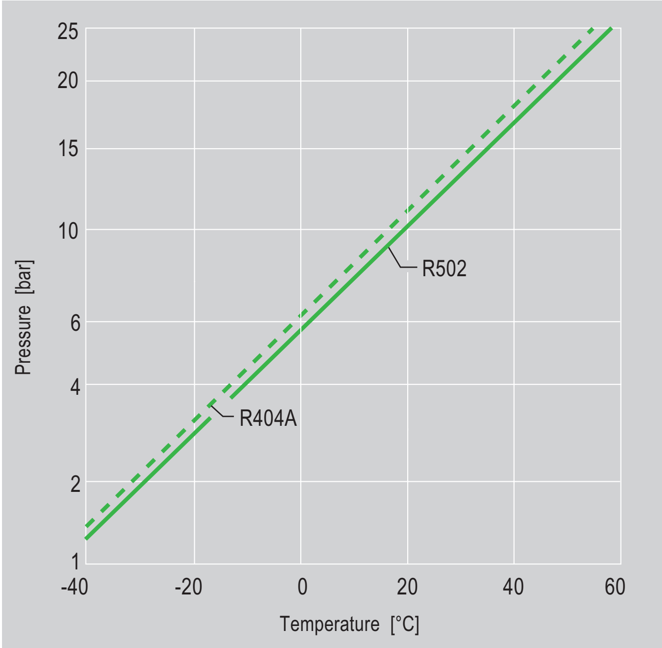


Fig. 12 Pressure level of R404A in comparison to R502

With regard to a uniform and easily comprehensible definition of the rated compressor capacity, the revised standards EN 12900 and AHRI540 are applied. Evaporating and condensing temperatures refer to saturated conditions (dew points).

- ❏ Evaporating temperature according to point A (Fig. 11)
- ❏ Condensing temperature according to point B (Fig. 11)

In this case the assessment of the effective superheat and subcooling temperatures will be simplified.

It must however be considered that the actual refrigerating capacity* of the system can be higher than the rated compressor capacity. This is partly due to an effectively lower temperature at the evaporator inlet.

A further characteristic of zeotropic refrigerants is the potential concentration shift when leakage occurs. Refrigerant loss in the pure gas and liquid phases is mainly non-critical. Leaks in the phase change areas, e.g. after the expansion valve, within the evaporator and condenser/receiver are considered more significant. It is therefore recommended that soldered or welded joints should be used in these sections.

Extended investigations have shown in the meantime that leakage leads to less serious changes in concentration than initially thought. In any case it is certain that the following substances of safety group A1 (see page 42) which are dealt with here cannot develop any flammable mixtures, either inside or outside the circuit. Essentially similar operating conditions and temperatures as before can be obtained by supplementary charging with the original refrigerant in the case of a small temperature glide.

Further conditions/recommendations concerning the practical handling of blends must also be considered:

- ❏ The plant always has to be charged with liquid refrigerant. When vapour is taken from the charging cylinder, concentration shifts may occur.
- ❏ Since all blends contain at least one flammable component, the entry of air into the system must be avoided. If the proportion of air is too high, a critical shift of the ignition point can occur under high pressure and while evacuating.
- ❏ The use of blends with a significant temperature glide is not recommended for plants with flooded evaporators. A large concentration shift is to be expected in this type of evaporator, and as a result also in the circulating refrigerant mass flow.

* In the new edition (2020) of the standard for condensing units EN13215, the declaration of performance data based on the mean evaporating temperature has also been included. This enables a direct comparison with performance data for single-component refrigerants.

Service blends with the basic component R22* as substitutes for R502

As a result of the continued refurbishment of older installations, the importance of these refrigerants is clearly on the decline. For some of them, production has already been discontinued. However, because of the development history of service blends, these refrigerants will continue to be covered in this Report.

These refrigerants belong to the group of "Service blends" and have been offered under the designations R402A/R402B* (HP80/HP81 – DuPont), R403A/R403B* (formerly ISCEON® 69S/69L) and R408A* ("Forane®" FX10 – Arkema).

The basic component is in each case R22, the high discharge gas temperature of which is significantly reduced by the addition of chlorine free substances with low isentropic compression exponent (e.g. R125, R143a, R218). A characteristic feature of these additives is an extraordinarily high mass flow, which enables the mixture to achieve a great similarity to R502.

R290 (Propane) is added as the third component to R402A/B and R403A/B to improve miscibility with traditional lubricants as hydrocarbons have especially good solubility characteristics.

For these blends two variations are offered in each case. When optimizing the blend variations with regard to identical refrigerating capacity as for R502 the laboratory measurements showed a significantly increased discharge gas temperature (Fig. 13), which above all, with higher suction gas superheat (e.g. supermarket use) leads to limitations in the application range.

On the other hand a higher proportion of R125 or R218, which has the effect of reducing the discharge gas temperature to the level of R502, results in somewhat higher refrigerating capacity (Fig. 14).

With regard to material compatibility the blends can be judged similarly to (H)CFC refrigerants. The use of conventional refrigeration oil (preferably semi or full synthetic) is also possible due to the R22 and R290 proportions.

Apart from the positive aspects there are also some disadvantages. These substances are alternatives only for a limited time. The R22 proportion has (although low) an ozone depletion potential. Furthermore, the additional components R125, R143a and R218 have a high global warming potential (GWP).

Resulting design criteria/ Converting existing R502 plants

The compressor and the components which are matched to R502 can remain in the system in most cases. The limitations in the application range must however be considered: Higher discharge gas temperature than R502 with R402B**, R403A** and R408A** or higher pressure levels with R402A** and R403B**.

The good solubility characteristics of R22 and R290 increase the risk that, after conversion of the plant, possible deposits of oil decomposition products containing chlorine are dissolved and find their way into the compressor and control devices. Systems where chemical stability was already insufficient with R502 operation (bad maintenance, low drier capacity, high thermal loading) are particularly at risk.

Thus, generously dimensioned suction gas filters and liquid line driers should be installed for cleaning before conversion, and an oil change should be made after approximately 100 hours operation. Further checks are recommended.

* When using blends containing R22, legal regulations are to be observed, see page 8.
** Classification according to ASHRAE nomenclature.

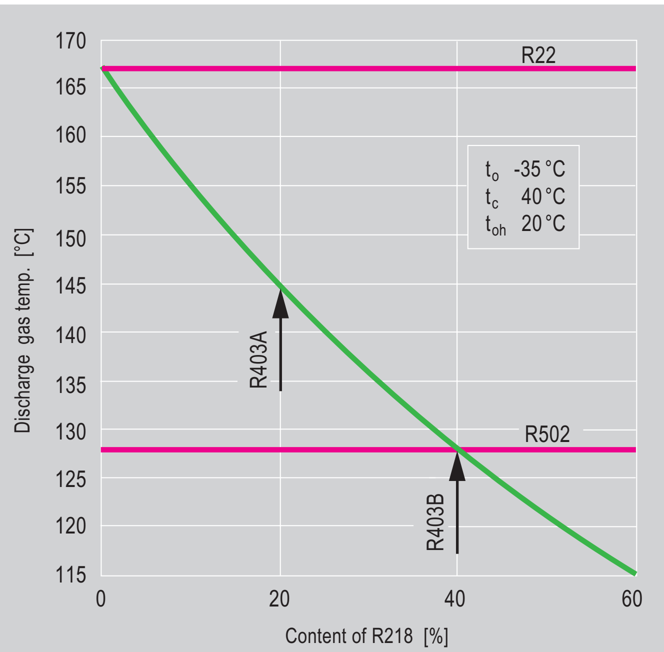


Fig. 13 Effect of the mixture variation upon the discharge gas temperature (example: R22/R218/R290)

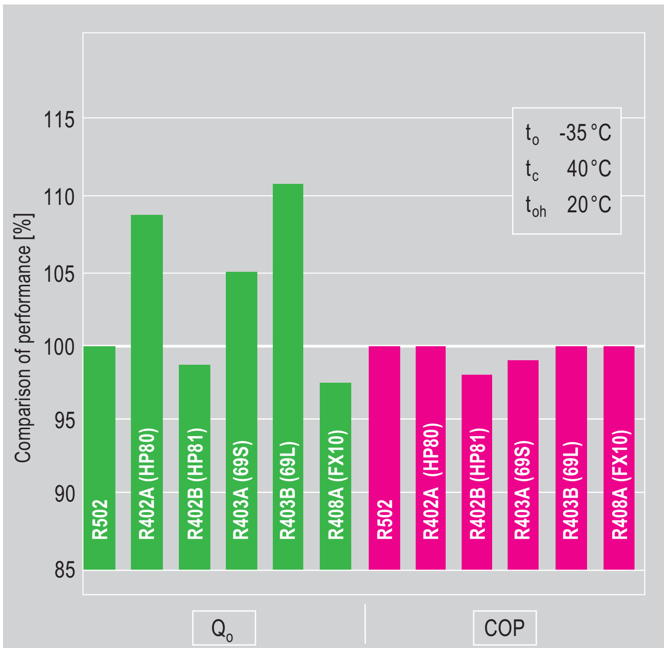


Fig. 14 Comparison of the performance data of a semi-hermetic compressor

The operating conditions with R502 (including discharge gas temperature and suction gas superheat) should be noted so that a comparison can be made with the values after conversion. Depending upon the results, control devices should possibly be reset and other additional measures should be taken as required.

Service blends as substitutes for R12 (R500)

Although (as experience already shows) R134a is also well suited for the conversion of existing R12 plants, the general use for such a "retrofit" procedure is not always possible. Not all compressors which have previously been installed are designed for the application with R134a. In addition a conversion to R134a requires the possibility to make an oil change, which is for example not the case with most hermetic type compressors.

Economical considerations also arise, especially with older plants where the effort of converting to R134a is relatively high. The chemical stability of such plants is also often insufficient and thus the chance of success is very questionable.

Therefore "Service blends" are also available for such plants as an alternative to R134a and are offered under the designations R401A/R401B, R409A. The main components are the HCFC refrigerants R22, R124 and/or R142b. Either HFC R152a or R600a (Isobutane) is used as the third component. Operation with traditional lubricants (preferably semi or full synthetic) is also possible due to the major proportion of HCFC.

A further service blend was offered under the designation R413A (ISCEON® 49 – DuPont), but replaced by R437A by the end of 2008. However, because of the development history of service blends, R413A will continue to be covered in this Report. The constituents of R413A consist of the chlorine free substances R134a, R218, and R600a. In spite of the high R134a content, the use of conventional lubricants is possible because of the relatively low polarity of R218 and the favourable solubility of R600a.

R437A is a blend of R125, R134a, R600 and R601 with similar performance and properties as R413A. This refrigerant is also chlorine-free (ODP = 0).

However, due to the limited miscibility of R413A and R437A with mineral and alkylbenzene oils, oil migration may result in systems with a high oil circulation rate and/or a large liquid volume in the receiver – for example if no oil separator is installed.

If insufficient oil return to the compressor is observed, the refrigerant manufacturer recommends replacing part of the original oil charge with ester oil. But from the compressor manufacturer's view, such a measure requires a very careful examination of the lubrication conditions. For example, if increased foam formation in the compressor crankcase is observed, a complete change to ester oil will be necessary. Moreover, under the influence of the highly polarized blend of ester oil and HFC, the admixture of or conversion to ester oil leads to increased dissolving of decomposition products and dirt in the pipework. Therefore, generously dimensioned suction clean-up filters must be provided. For further details, see the refrigerant manufacturer's "Guidelines".

Resulting design criteria/ Converting existing R12 plants

Compressors and components can mostly remain in the system. However, when using R413A and R437A the suitability must be checked against HFC refrigerants. The actual "retrofit" measures are mainly restricted to changing the refrigerant (possibly oil) and a careful check of the superheat setting of the expansion valve.

A significant temperature glide is present due to the relatively large differences in the boiling points of the individual substances, which requires an exact knowledge of the saturation conditions (can be found from vapour tables of refrigerant manufacturer and in the BITZER Refrigerant App) in order to assess the effective suction gas superheat.

In addition the application range must also be observed. Different refrigerant types are required for high and low evaporating temperatures or distinct capacity differences must be considered. This is due to the steeper capacity characteristic, compared to R12.

Due to the partially high proportion of R22 especially with the low temperature blends, the discharge gas temperature with some refrigerants is significantly higher than with R12. The application limits of the compressor should therefore be checked before converting.

The remaining application criteria are similar to those for the substitute substances for R502 which have already been mentioned.

* By using R22 containing blends the legal requirements are to be followed, see chapter R22 as transitional refrigerant, page 8.

R404A and R507A as substitutes for R22 and R502

These blends are chlorine free substitutes (ODP = 0) for R22 as well as for R502 in medium and low temperature ranges.

A composition which was already launched at the beginning of 1992 is known under the trade name Suva® HP62 (DuPont). Long term use has shown good results. Further blends were traded as Forane® FX70 (Arkema) and Genetron® AZ50 (Allied Signal/ Honeywell) or Solkane® 507 (Solvay). HP62 and FX70 have been listed in the ASHRAE nomenclature as R404A and AZ50 as R507A.

The basic components belong to the HFC group, where R143a belongs to the flammable category. Due to the combination with a relatively high proportion of R125 the flammability is effectively counteracted, even in the case of leakage.

A feature of all three ingredients is the very low isenropic compression exponent which results in a similar, with even a tendency to be lower, discharge gas temperature to R502 (Fig. 15). The efficient application of single stage compressors with low evaporating temperatures is therefore guaranteed.

Due to the similar boiling points for R143a and R125, with a relatively low proportion of R134a, the temperature glide with the ternary blend R404A within the relevant application range is less than one Kelvin. The characteristics within the heat exchangers are therefore not very different than with azeotropes. The results obtained from heat transfer measurements show favourable conditions.

R507A is a binary substance combination which even gives an azeotropic characteristic over a relatively wide range. The conditions therefore tend to be even better.

The performance (Fig. 16) gives hardly any difference between the various substances and ist very similar to R502. This also explains the high market penetration of these refrigerants. With regard to the thermodynamic properties, they are particularly suitable for commercial medium and low temperature systems.

Typical metallic materials are compatible with HFC refrigerants. Elastomers, however, must be adapted to the changed characteristics. Suitable lubricants are polyol esters (see chapter Lubricants for compressors, page 41).

The relatively high global warming potential (GWP = 3922 .. 3985), which is mainly determined by the R143a and R125, is something of a hitch. However, it is better than R502 and with regard to the favourable energy demand also leads to a reduction of the TEWI value. Other improvements are possible in this respect due to further developed system control.

Nevertheless, due to their high global warming potential (GWP), the use of R404A and R507A is no longer allowed in the EU in new installations since 2020. This has been settled in the F-Gas Regulation No. 517/2014 to be applied since 2015. However, the current requirement of phase-down in connection with a strict quota system has already led to an earlier phase-out in many applications. For more detailed information, please refer to BITZER brochure A-510.

In the USA, Canada and Australia there are also requirements to phase-out R404A and R507A. For an international phase-down (since 2019) of HCFC and HFC refrigerants, the so-called Kigali Amendment was agreed upon in 2016 as part of the Montreal Protocol.

Alternatives with lower GWP are the HFC blends explained in the following as well as the newly developed HFO/HFC blends (from page 24).

Halogen free refrigerants or cascade systems using different refrigerants are also an option for specific applications (from page 28).

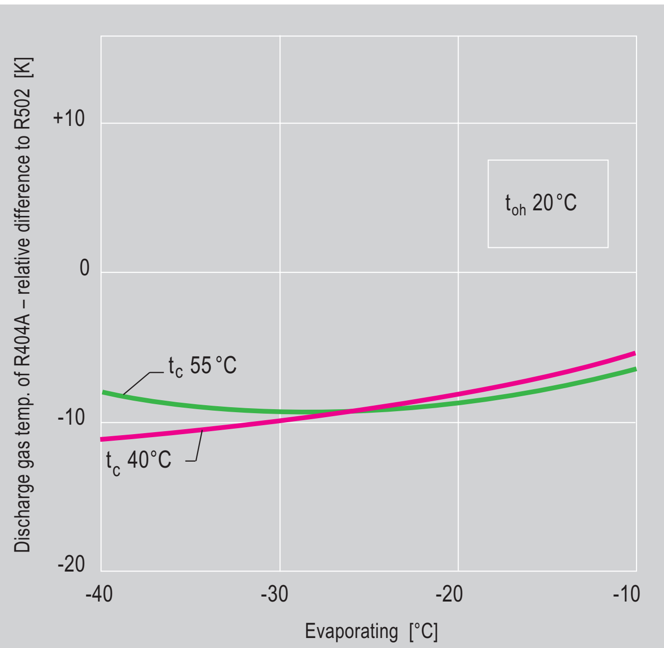


Fig. 15 R404A/R502 – comparison of discharge gas temperatures of a semi-hermetic compressor

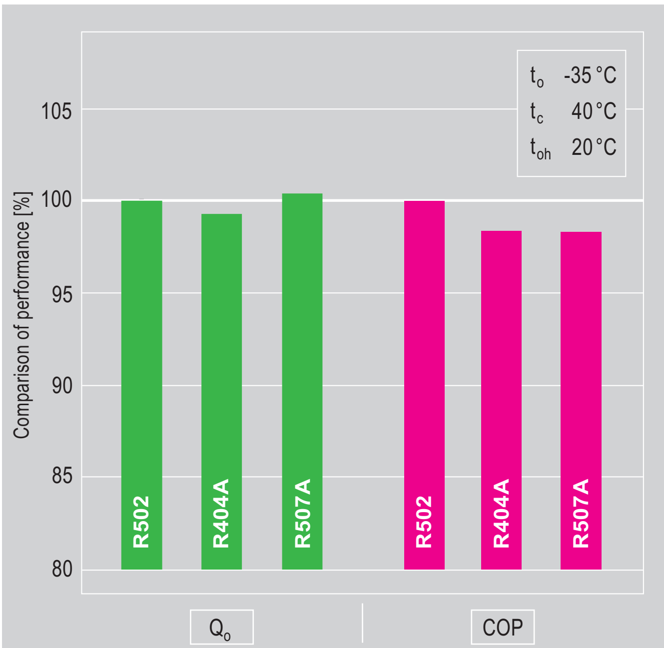


Fig. 16 Comparison of performance data of a semi-hermetic compressor

Resulting design criteria

The system technology can be based on the experience with R22 and R502 over a wide area.

On the thermodynamic side, a heat exchanger between the suction and liquid line is recommended as this will improve the refrigerating capacity and COP.

BITZER offers the whole program of reciprocating, scroll and screw compressors for R404A and R507A.

Supplementary BITZER information concerning the use of HFC blends (see also https://www.bitzer.de)

- ❑ **Technical Information A-540 „Retrofit R22 or R404A/R507A – Step by step"**
- ❑ **Technical Information KT-500 „BITZER refrigeration compressor oils for reciprocating compressors"**

R407A/407B/407F/407H as substitutes for R22 and R502

As an alternative to the earlier described substitutes, additional mixtures have been developed based on R32 which is chlorine free (ODP = 0) and flammable like R143a. The refrigerant R32 is also of the HFC type and initially was regarded as a main candidate for R22 alternatives (page 20). However, due to extent of blend variations comparable thermodynamic characteristics to R404A/R507A can also be obtained.

These kind of refrigerants were marketed at first under the trade name KLEA® 60/61 (ICI) and are listed as R407A/R407B* in the ASHRAE nomenclature.

Honeywell has developed another blend with the trade name Performax® LT (R407F according to ASHRAE nomenclature) and introduced it into the market, similar Daikin Chemical with R407H. For both blends, the R32 proportion is higher than for R407A, while the R125 proportion is lower. With R407H, this results in certain restrictions for low temperature applications.

However, the necessary conditions for alternatives containing R32 are not quite as favourable compared to the R143a based substitutes discussed earlier. The boiling point of R32 is very low at -52°C, in addition the isentropic compression exponent is even higher than with R22. Rather high proportions of R125 and R134a are necessary to match the characteristics at the level of R404A and R507A. The flammability of R32 is thus effectively suppressed, but the large differences in boiling points with a high proportion of R134a lead to a larger temperature glide.

The main advantage of R32 is the relatively low global warming potential (GWP = 675), so that even in combination with R125 and R134a it is significantly lower than with the R143a based alternatives mentioned above (R407A: GWP = 2107, R407F: GWP = 1825, R407H: GWP = 1490).

Thus, they also comply with the requirement of the new EU F-Gas Regulation which from 2020 will only allow refrigerants of GWP < 2500.

Measurements made with R32 containing blends do show certain capacity reductions compared to R404A and R507A, with low evaporating temperatures. The COP however shows less deviation and is even higher in medium temperature applications (Fig. 18).

* Meanwhile, R407B is no longer available in the market. Due to the historical development of HFC blends this refrigerant will, however, still be considered in this Report.

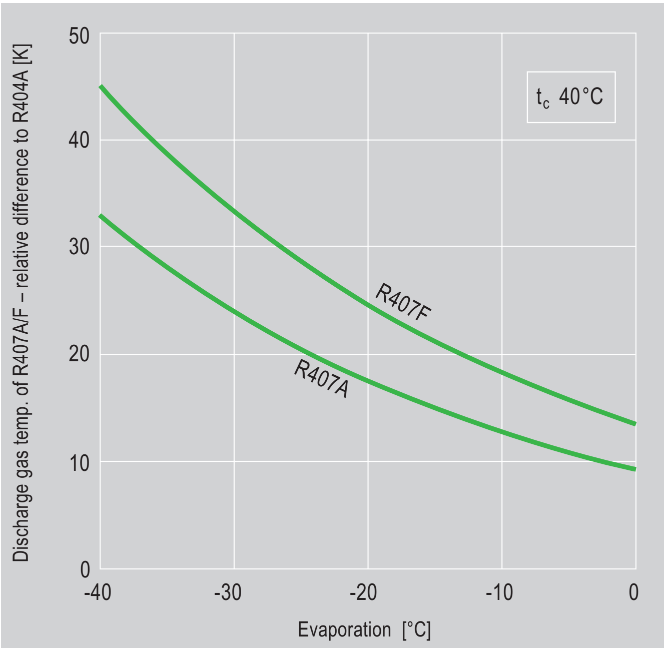


Fig. 17 R407A, R407F/R404A – comparison of discharge gas temperature of a semi-hermetic compressor

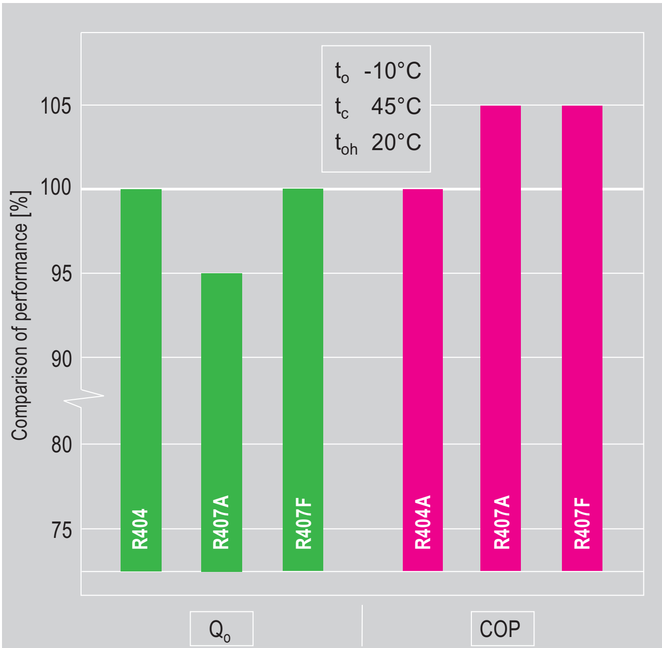


Fig. 18 Comparison of performance data of a semi-hermetic compressor

Whether these favourable conditions are confirmed in real applications is subject to the system design. An important factor is the significant temperature glide, which can have a negative influence upon the capacity/temperature difference of the evaporator and condenser.

With regard to the material compatibility, R32 blends can be assessed similarly to R404A and R507A; the same applies to the lubricants.

Despite the relatively high proportion of R125 and R134a in the R32 blends, the discharge gas temperature is higher than with the R143a based alternatives (especially for R407F and even to a higher degree with R407H). This results in certain limitations in the application range as well as the requirement for additional cooling of compressors when operating at high pressure ratios.

2-stage compressors can be applied very efficiently where especially large lift conditions are found. An important advantage in this case is the use of a liquid subcooler.

Resulting design criteria

The experience with R404A/R507A and R22 can be used for plant technology in many respects, although the temperature glide as well as the difference in the thermodynamic properties have to be considered. This especially concerns the design and construction of heat exchangers and expansion valves.

Converting existing R22 plants to R407A/407B/407F/407H

Practical experiences show that qualified conversions are possible. Compared to R22 the volumetric refrigeration capacity is nearly similar while the refrigerant mass flow is only slightly higher. These are relatively favourable conditions for the conversion of medium and low temperature R22 systems.

The main components can remain in the system provided that they are compatible with HFC refrigerants and ester oils.

However, special requirements placed on the heat exchanger with regard to the significant temperature glide must be considered. A conversion to ester oil is also necessary, which leads to increased dissolving of decomposition products and dirt in the pipework. Therefore, generously dimensioned suction clean-up filters must be provided.

Conversion of existing R404A/R507A systems to R407A/407B/407F/407H

Larger differences in thermodynamic properties (e.g. mass flow, discharge gas temperature) and the temperature glide of R407A/F/H may require the replacement of control components and if necessary retrofitting of additional compressor cooling when existing systems are converted.
For newly built systems, a specific design of components and system is necessary.

BITZER offers a comprehensive program of reciprocating and screw compressors for R407A and R407F. An individual selection of compressors for R407H is possible upon demand.

R422A as substitute for R22 and R502

Amongst other aims, R422A (ISCEON® MO79 – Chemours) was developed in order to obtain a chlorine-free refrigerant (ODP = 0) for the simple conversion of existing medium and low temperature refrigeration systems using R22 and R502.

For this, it was necessary to formulate a refrigerant with comparable performance and energy efficiency to that of R404A, R507A, and R22, which also permits the use of conventional lubricants.

R422A is a zeotropic blend of the basic components R125 and R134a with a small addition of R600a. Due to its relatively high R134a percentage, the temperature glide (see chapter Refrigerant Properties, page 42) lies higher than for R404A, but lower than other refrigerants with the same component blends – such as R417A and R422D (see page 22).

The adiabatic exponent, and therefore also the discharge gas and oil temperatures of the compressor, are lower than for R404A and R507A. At extremely low temperatures, this can be advantageous. However, in cases of low pressure ratio and suction gas superheat, this can be a disadvantage due to increased refrigerant solution if ester oil is used.

The material compatibility is comparable to the blends mentioned previously, the same applies to the lubricants. On account of the good solubility of R600a, conventional lubricants can also be used under favourable circumstances.

In particular, advantages result during the conversion of existing R22 and R502 systems as mentioned above. However, for plants with high oil circulation rates and/or large liquid charge in the receiver, oil migration might occur – for example if no oil separator is installed.

If insufficient oil return to the compressor is observed, the refrigerant manufacturer recommends replacing part of the original oil charge with ester oil. But from the compressor manufacturer's view, such a measure requires a very careful examination of the lubrication conditions. For example, if increased foam formation in the compressor crankcase is observed, a complete change to ester oil* will be necessary. Under the influence of the highly polarized blend of ester oil and HFC, the admixture of or conversion to ester oil leads to increased dissolving of decomposition products and dirt in the pipework. Therefore, generously dimensioned suction clean-up filters must be provided. For further details, see the refrigerant manufacturer's "Guidelines".

From a thermodynamic point of view, a heat exchanger between suction and liquid line is recommended, improving the refrigerating capacity and coefficient of performance. Besides this the resulting increase in operating temperatures leads to more favourable lubricating conditions (lower solubility).

Due to the high global warming potential (GWP ≥ 2500), R422A will no longer be allowed for new installations in the EU from 2020 onwards. The requirements and restrictions are specified in the F-Gas Regulation 517/2014.

* General proposal for screw compressors and liquid chillers when used with DX evaporators with internally structured heat exchanger tubes. Furthermore, an individual check regarding possible additional measures will be necessary.

BITZER compressors are suitable for R422A. An individual selection is possible upon demand.

Substitutes for R22 in air conditioning systems and heat pumps

As the HCFC refrigerant R22 (ODP = 0.05) is accepted only as a transitional solution, a number of chlorine-free (ODP = 0) alternatives have been developed and tested extensively. They are being used for a large range of applications.

Experience shows, however, that none of these substitutes can replace the refrigerant R22 in all respects. Amongst others there are differences in the volumetric refrigerating capacity, restrictions in possible applications, special requirements in system design and considerably differing pressure levels. According to the specific operating conditions, various alternatives may be considered.

Apart from the single-component HFC refrigerant R134a, these are mainly blends (different compositions) of the components R32, R125, R134a, R143a, and R600(a). The following description mainly concerns the development and potential applications of these. The halogen-free substitutes NH_3, propane and propylene as well as CO_2 should also be considered, however, specific criteria must be applied for their use (description from page 28).

In addition, R32 and HFO/HFC blends can also be used as alternatives (see chapter R32 as substitute for R22 and HFO/HFC blends, from page 23).

R407C as substitute for R22

Mixtures of HFC refrigerants R32, R125 and R134a were considered to be the preferred candidates for short-term substitutes for R22 in the EU in view of the early ban of R22. Performance values and efficiency are highly comparable (Fig. 19).
At first two blends of the same composition have been introduced under the trade names AC9000* (DuPont) and KLEA® 66* (ICI). They are listed in the ASHRAE nomenclature as R407C. In the meantime there are also further blend varieties (e.g. R407A/R407F/R407H) with somewhat differing compositions, whose properties have been optimized for particular applications (see page 18).

Unlike the substitutes for R22 in refrigeration systems with identical blend components (pages 18 and 19), the substitutes for R22 in air conditioning systems and heat pumps under consideration contain higher proportions of R32 and R134a. A good correspondence with the properties of R22 in terms of pressure levels, mass flow, vapour density and volumetric refrigerating capacity is thus achieved. In addition, the global warming potential is relatively low (GWP = 1774).

Thus, R407C also complies with the requirement of the new EU F-Gas Regulation which from 2020 onwards will only allow refrigerants with GWP < 2500. However, the quantity limitation through the "phase-down" will also lead to significantly restricted availability.

The high temperature glide is a disadvantage for usual applications which requires appropriate system design and can have a negative influence on the efficiency of the heat exchangers (see chapter General characteristics of zeotropic blends, page 13).

Due to the properties mentioned, R407C is preferably an R22 substitute for air conditioning and heat pump systems and (within certain limitations) also for medium temperature refrigeration. In low temperature refrigeration, because of the high proportion of R134a, a significant drop in refrigerating capacity and COP is to be expected. There is also the danger of an increased R134a concentration in the blend in evaporators, with reduced performance and malfunctioning of the expansion valve (e.g. insufficient suction gas superheat).

Material compatibility is similar to that of the blends discussed previously; the same applies to lubricants.

* Previous trade names are not used any more.

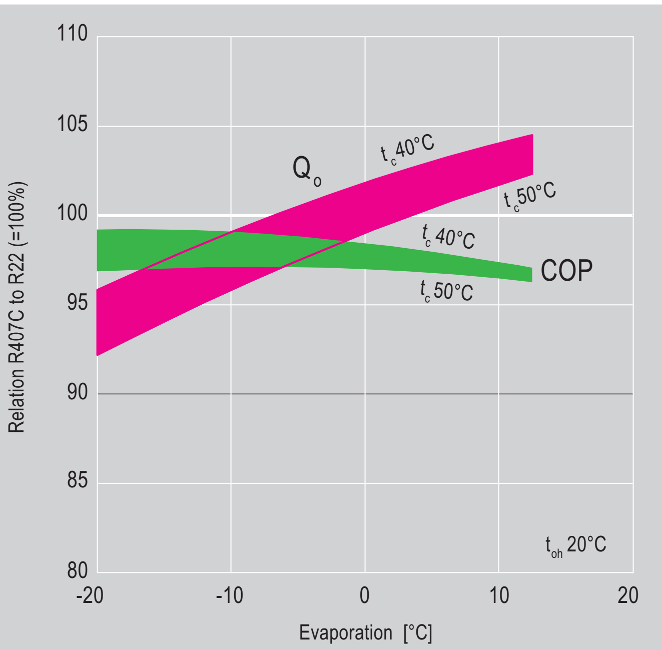


Fig. 19 R407C/R22 – comparison of performance data of a semi-hermetic compressor

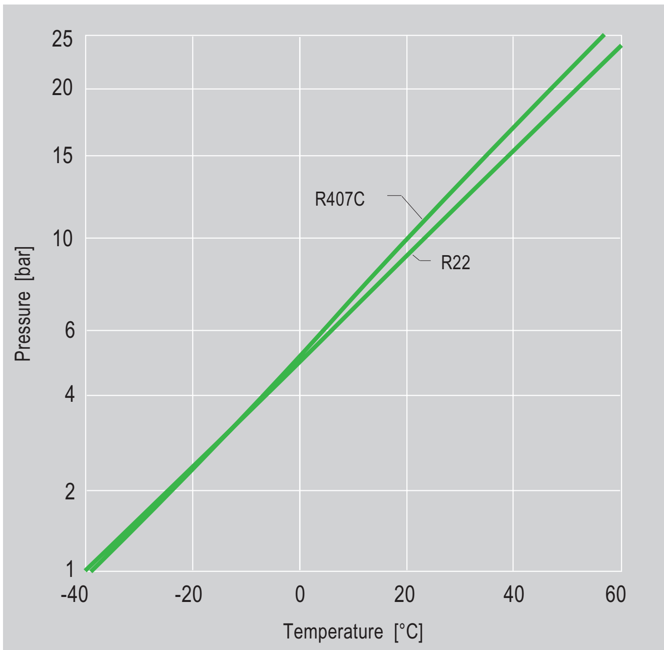


Fig. 20 R407C/R22 – comparison of pressure levels

Resulting design criteria

With regard to system technology, previous experience with R22 can only be utilized to a limited extent.

The distinctive temperature glide requires a particular design of the main system components, e.g. evaporator, condenser, expansion valve. In this context it must be considered that heat exchangers should preferably be laid out for counterflow operation and with optimized refrigerant distribution. There are also special requirements with regard to the adjustment of control devices and service handling.

Furthermore, the use in systems with flooded evaporators is not recommended as this would result in a severe concentration shift and layer formation in the evaporator.

BITZER can supply a widespread range of semi-hermetic reciprocating, screw and scroll compressors for R407C.

Converting existing R22 plants to R407C

Because of the above mentioned criteria, no general guidelines can be defined. Each case must be examined individually.

R410A as substitute for R22

In addition to R407C, the near-azeotropic mixture listed by ASHRAE as R410A is available and widely used for medium-sized capacities in air conditioning and heat pump applications.

An essential feature indicates nearly 50% higher volumetric refrigerating capacity (Fig. 21) compared to R22, but with the consequence of a proportional rise in system pressures (Fig. 22).

At high condensing temperatures, energy consumption/COP initially seems to be less favourable than with R22.

This is mainly due to the thermodynamic properties. On the other hand, very high isentropic efficiencies are achievable (with reciprocating and scroll compressors), so that the real differences are lower.

Another aspect are the high heat transfer coefficients in evaporators and condensers determined in numerous test series, resulting in especially favourable operating conditions. With an optimized design, it is quite possible for the system to achieve a better overall efficiency than with other refrigerants.

Because of the negligible temperature glide (< 0.2 K), the general usability is similar to that of a pure refrigerant.

The material compatibility is comparable to the previously discussed blends, the same applies to the lubricants. However, the pressure levels and the higher specific loads on the system components need to be taken into account.

Resulting design criteria

The fundamental criteria for HFC blends also apply to the system technology with R410A. However, the high pressure levels have to be considered (43°C condensing temperature already corresponds to 26 bar abs.).

Compressors and other system components designed for R22 are not suitable for this refrigerant (or only to a limited extent).

Though, suitable compressors and system components are available.

When considering to cover usual R22 application ranges, the significant differences in the thermodynamic properties (e.g. pressure levels, mass and volume flow, vapour density) must be taken into account. This also requires considerable constructional

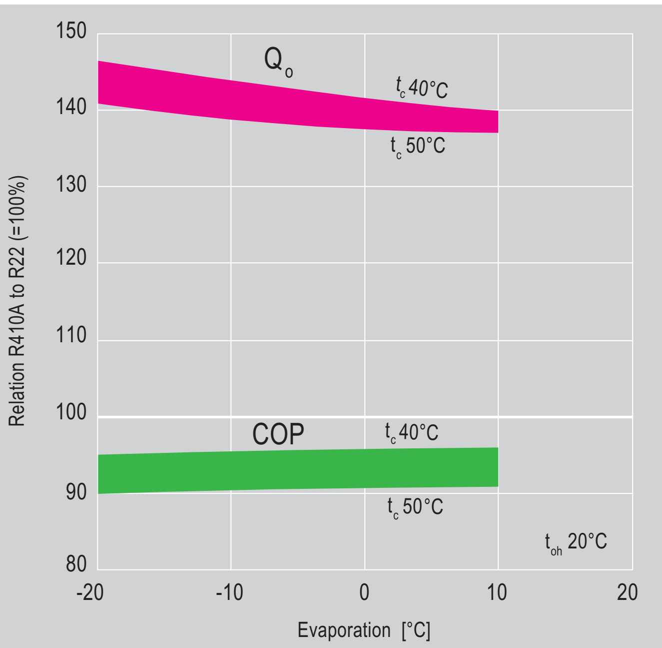


Fig. 21 R410A/R22 – comparison of performance data of a semi-hermetic compressor

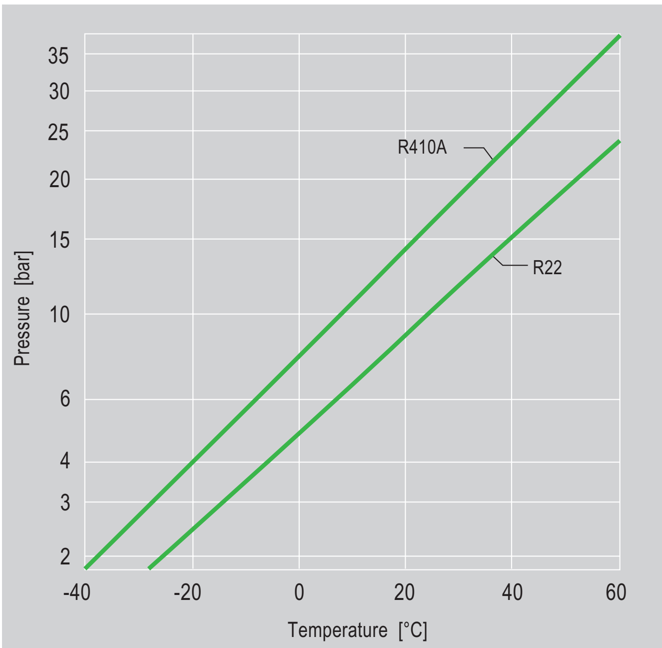


Fig. 22 R410A/R22 – comparison of pressure levels

changes to compressors, heat exchangers, and controls, as well as measures of tuning vibrations. There are stricter safety requirements, e.g. affecting the quality and dimensions of piping and flexible tube elements (for condensing temperatures of approx. 60°C/40 bar).

Another criterion is the relatively low critical temperature of 71°C. Irrespective of the design of components on the high pressure side, the condensing temperature is thus limited.

R410A complies with the requirements of the EU F-Gas Regulation, which will only allow refrigerants with GWP < 2500 from 2020 onwards. However, the quantity limitation through the "phase-down" will also lead to significantly restricted availability. Due to the extremely high demand for R410A, a timely switch to alternatives is needed in the EU.

For R410A, BITZER offers a series of semi-hermetic reciprocating compressors and scroll compressors.

R417A/417B/422D/438A as substitutes for R22

Similar to the development of R422A (page 19), one aim of developing these blends was to provide chlorine-free refrigerants (ODP = 0) for the simple conversion of existing R22 plants.

R417A was introduced to the market years ago, and is also offered under the trade name ISCEON® MO59 (Chemours). This substitute for R22 contains the blend components R125/R134a/R600 and therefore differs considerably from e.g. R407C with a correspondingly high proportion of R32.

Meanwhile, a further refrigerant based on identical components, but with a higher R125 content, has been offered under the ASHRAE designation R417B. Due to its lower R134a content, its volumetric refrigerating capacity and pressure levels are higher than for R417A. This results in different performance parameters and a different focus within the application range.

The same applies to a further blend with the same main components, but R600a as hydrocarbon additive. It is offered under trade name ISCEON® MO29 (Chemours) and listed as R422D in the ASHRAE nomenclature.

Another refrigerant belonging to the category of HFC/HC blends was introduced in 2009 under the trade name ISCEON® MO99 (Chemours) – ASHRAE classification R438A. This formulation was designed especially for a higher critical temperature for applications in hot climate areas. The base components are R32, R125, R134a, R600 and R601a.

Like R407C, all four substitute refrigerants are zeotropic blends with a more or less significant temperature glide. In this respect, the criteria described for R407C also apply here.

Apart from a similar refrigeration capacity, there are nevertheless fundamental differences in thermodynamic properties and in oil transport behaviour. The high proportion of R125 causes a higher mass flow with R417A/B and R422D than with R407C, a lower discharge gas temperature and a relatively high superheating enthalpy. These properties indicate that there are differences in the optimization of system components, and a heat exchanger between liquid and suction lines is of advantage.

Despite the predominant proportion of HFC refrigerants, conventional lubricants can be used to some extent because of the good solubility of the hydrocarbon constituent. However, in systems with a high oil circulation rate and/or a large volume of liquid in the receiver, oil migration may result.

In such cases, additional measures are necessary. For further information on oil return and lubricants see chapter “R422A as substitute for R22 and R502” (page 19).

Due to the high global warming potential (GWP ≥ 2500), R417B and R422D will no longer be allowed for new installations in the EU from 2020. The requirements and restrictions are specified in the F-Gas Regulation 517/2014. However, the "phase-down" quantity limitation will also lead to significantly restricted availability of R417A and R438A.

BITZER compressors are suitable for use with R417A/417B/422D/438A. An individual selection is possible upon request.

R427A as a substitute for R22

This refrigerant blend was introduced some years ago under the trade name Forane® FX100 (Arkema) and is now listed in the ASHRAE nomenclature as R427A.

The R22 substitute is offered for the conversion of existing R22 systems for which a "zero ODP" solution is requested. It is an HFC mixture with base components R32/R125/R143a/R134a.

In spite of the blend composition based on pure HFC refrigerants, the manufacturer states that a simplified conversion procedure is possible.

This is facilitated by the R143a proportion. Accordingly, when converting from R22 to R427A, all it takes is a replacement of the original oil charge with ester oil. Additional flushing sequences are not required, as proportions of up to 15% of mineral oil and/or alkyl benzene have no significant effect on oil circulation in the system.

However, it must be taken into account that the highly polarized mixture of ester oil and HFC will lead to increased dissolving of decomposition products and dirt in the pipework. Therefore, generously dimensioned suction clean-up filters must be provided.

Regarding refrigerating capacity, pressure levels, mass flow and vapor density, R427A is relatively close to R22. During retrofit, essential components such as expansion valves can remain in the system. Due to the high proportion of blend components with low adiabatic exponent, the discharge gas temperature is considerably lower than with R22, which has a positive effect at high compression ratios.

It must be taken into account that this is also a zeotropic blend with a distinct temperature glide. Therefore the criteria described for R407C apply here as well.

R427A meets the requirement of the EU F-Gas Regulation, which will only allow refrigerants with GWP < 2500 from 2020. However, the quantity limitation due to the "phase-down" will also lead to significantly restricted availability.

BITZER compressors are suitable for R427A. An individual selection is possible upon demand.

Supplementary information concerning the use of HFC blends
(see also https://www.bitzer.de)

- ❑ **Technical information A-540 "Retrofit R22 or R404A/R507A – Step by step"**

R32 as substitute for R22

As described earlier, R32 belongs to the HFC refrigerants, but initially it was mainly used as a component of refrigerant blends only. An essential barrier for the application as a pure substance so far is the flammability. This requires adequate charge limitations and/or additional safety measures, especially with installations inside buildings. In addition there are very high pressure levels and discharge gas temperatures (compression exponent higher than with R22 and R410A).

On the other hand, R32 has favorable thermodynamic properties, e.g. very high evaporating enthalpy and volumetric refrigerating capacity, low vapor density (low pressure drop in pipelines), low mass flow, and favorable power input for compression. The global warming potential is relatively low (GWP = 675).

Looking at these favorable properties and taking into account the additional effort for emission reductions, R32 will increasingly be used as a refrigerant in factory produced systems (A/C units, liquid chillers, heat pumps).

It was proven in flammability tests that the necessary ignition energy is very high and the flame speed is low. Therefore, R32 (like R1234yf and R1234ze) has been placed in the new safety group A2L according to ISO 817.

The resulting safety requirements are specified in the revised EN 378 (amended version 2016).

R32 is also considered an alternative for systems with larger refrigerant charge, e.g. liquid chillers for air conditioning and process applications and heat pumps previously operated with R410A. However, depending on the installation site of the system, appropriate refrigerant charge limits must be observed. On the other hand, there are no such restrictions when installed outdoors (without access to unauthorized persons) and in machine rooms (for example, according to EN 378-3: 2016). It should be noted, however, that R32 precharged chillers may be subject to special conditions during transport (according to the Pressure Equipment Directive, R32 is classified under Fluid Group 1).

BITZER scroll compressors of the ORBIT GSD6..AL and GSD8..AL series have been approved and released for use with R32.

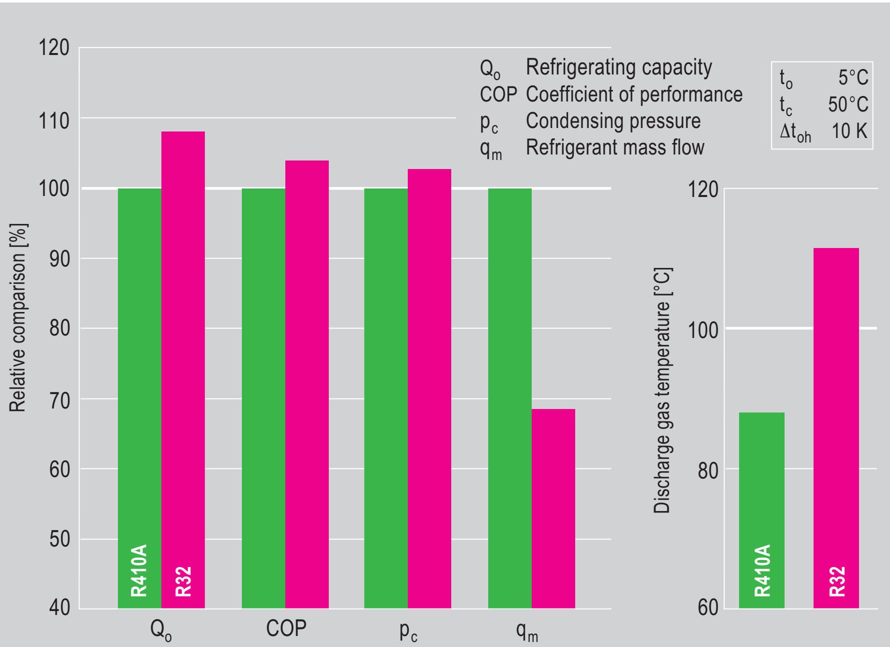


Fig. 23 R32/R410A – comparison of performance and operating data of a scroll compressor

"Low GWP" HFOs and HFO/HFC blends as alternatives to HFCs

The decision to use the "low GWP" refrigerant R1234yf in mobile air conditioning systems for passenger cars (see pages 11/12) also led to the development of alternatives for further mobile applications as well as stationary refrigeration, air conditioning and heat pump systems.

Primary objectives are the use of single-component refrigerants and of mixtures with significantly reduced GWP and similar thermodynamic properties as the HFCs currently used predominantly.

An essential basic component for this is R1234yf ($CF_3CF=CH_2$). This refrigerant belongs to the group of hydro-fluoro-olefins (HFO), i.e. unsaturated HFCs with molecular double bonds. This group of HFOs also includes another substance called R1234ze(E), which has been mainly used as a propellant for PU foam and aerosol. R1234ze(E) ($CF_3CH=CFH$) differs from R1234yf in its molecular structure.

Both substances are the preferred choice in terms of their properties and are also used as basic components in HFO/HFC blends. The Global Warming Potential is very low − R1234yf with GWP 4 and R1234ze(E) with GWP 7. However, these refrigerants are flammable (safety class A2L), meaning the refrigerant quantity in the system must be considered in light of the installation location. In addition, there remain open questions concerning the long-term stability in stationary systems where long life cycles are common. Furthermore the volumetric refrigerating capacity is relatively low; for R1234yf it is close to the level of R134a, and more than 20% lower for R1234ze(E).

There is also some uncertainty concerning flammability. In safety data sheets, R1234ze(E) is declared as non-flammable. However, this only applies to its transport and storage. When used as a refrigerant, a higher reference temperature for flammability tests of 60°C applies. At this temperature, R1234ze(E) is flammable and therefore classified in safety class A2L, like R1234yf.

R1234ze(E) is sometimes referred to as a R134a substitute, but its volumetric refrigerating capacity is more than 20% lower than that of R134a or R1234yf. The boiling point (-19°C) also greatly restricts the application at lower evaporation temperatures. Its preferred use is therefore in liquid chillers and high temperature applications. For further information see chapter Refrigerants for special applications, page 37.

The list of further potential HFO refrigerants is relatively long. However, there are only few fluids that meet the requirements in terms of thermodynamic properties, flammability, toxicity, chemical stability, compatibility with materials and lubricants. These include e.g. the non-flammable (safety group A1) low-pressure refrigerants R1224yd(Z), R1233zd(E), R1336mzz(E), R1336mzz(Z) and R514A (blend of R1336mzz(Z)/R1130(E)). These are primarily an option for liquid chillers with large turbo-compressors, and they can be used with positive displacement compressors in high-temperature applications as well as ORC systems. Further information: see chapter Refrigerants for special applications, page 37.

R1224yd(Z) and R1233zd(E) belong to the group of HCFO (hydro-chloro-fluoro-olefins); they have a (very) low ozone depletion potential (ODP). Upon release into the atmosphere, however, the molecule rapidly disintegrates.

On the other hand, there are currently no candidates from the HFO family with similar volumetric refrigerating capacity such as R22/R407C, R404A/R507A and R410A available for commercial use. Direct alternatives for these refrigerants with significantly lower GWPs must therefore be "constructed" as a mixture of R1234yf and/or R1234ze(E) with HFC refrigerants, possibly also small proportions of hydrocarbons, CO_2 or other suitable molecules.

However, due to the properties of the HFC refrigerants suitable as blend components, flammability and GWP are related diametrically to one another. In other words: Blends as alternatives to R22/R407C of GWP < approx. 900 are flammable. This is also true with alternatives for R404A/R507A in blends of GWP < approx. 1300 and for R410A in blends of GWP < approx. 2000. The reason for this is the high GWP of each of the required non-flammable components. There are a few exceptions, which are discussed in chapter Further development projects with "Low GWP" refrigerants, page 26.
For R134a alternatives, the situation is more favorable. Due to the already quite low GWP of R134a, a blend with R1234yf and/or R1234ze(E) allows a formulation of non-flammable refrigerants with a GWP of approx. 600.

Thus, primarily two directions for development are pursued:
- ❏ Non-flammable HFC alternatives (blends) with GWP values according to the above mentioned limits – safety group A1. Regarding safety requirements, these refrigerants can then be utilized similar to currently used HFCs.
- ❏ Flammable HFC alternatives (blends) with GWP values below the above mentioned possible limits – according to safety group A2L (for refrigerants of lower flammability).

This group of refrigerants is then subject to charge limitations according to future requirements for A2L refrigerants.

Meanwhile, there are development projects using refrigerant components with a much higher volumetric refrigerating capacity and pressure than R1234yf and R1234ze(E). These can then be used to "formulate" mixtures with R32 as an alternative to R410A, which are optimised for certain properties. See additional information in chapter Further development projects with "Low GWP" refrigerants, page 26.

R134a alternatives

In addition to the flammable HFO refrigerants R1234yf and R1234ze(E) already described, non-flammable mixtures are now also available as R134a alternatives. As previously mentioned, the initial situation is most favorable for these.

They achieve GWP values of approx. 600 − less than half of R134a (GWP = 1430). In addition, this type of blends can have azeotropic properties, so that they can be used like pure refrigerants.

For quite some time a blend has been applied on a larger scale in real systems – this was developed by Chemours and is called Opteon™ XP-10. Results available today are highly satisfactory.

This is also true for an R134a alternative designated Solstice® N-13 and offered by Honeywell which, however, differs regarding the blend composition.

The refrigerants are listed in the ASHRAE nomenclature under R513A (Chemours) and R450A (Honeywell).

The same category also includes the refrigerant blends R516A (ARKEMA ARM 42) as well as R456A (Koura/Mexichem AC5X).

All options show refrigerating capacity, power input, and pressure levels similar to R134a. Thus, components and system technology can be taken over, only minor changes like superheat adjustment of the expansion valves are necessary.

Polyolester oils are suitable lubricants which must meet special requirements, e.g. for the utilization of additives.

Prospects are especially favorable for supermarket applications in the medium temperature range in a cascade with CO_2 for low temperature, just as in liquid chillers with higher refrigerant charges where the use of flammable or toxic refrigerants would require comprehensive safety measures.

A special case is the refrigerant R515B: an azeotropic mixture of R1234ze(E) and small amounts of R227ea. This combination, declared by the manufacturer Honeywell as an R134a alternative, is non-flammable (A1) despite the very low GWP of approx. 300.

However, as with the previously described R1234ze(E), this can only be considered an alternative under certain restrictions. The volumetric refrigerating capacity is also more than 20% lower than that of R134a or R1234yf.

This category of substitutes also includes R471A (Honeywell), a blend of R1234ze(E), R1336mzz(E) and R227ea. R1336mzz(E) is a non-flammable HFO low-pressure refrigerant which can also be used with turbo compressors and for high temperature heat pumps. Due to the two main HFO components, the GWP of the blend is < 150, but it is still non-flammable (A1).

A disadvantage, however, is the even lower volumetric refrigerating capacity compared to R515B.

Substitutes for R404A/R507A and R410A

Since the available HFO molecules (R1234yf and R1234ze) show a considerably smaller volumetric refrigerating capacity than the above mentioned HFC refrigerants, relatively large HFC proportions with high volumetric refrigerating capacity must be added for the particular alternatives. The potential list of candidates is rather limited, one option is R32 with its relatively low GWP of 675.

However, one disadvantage is its flammability (A2L), resulting also in a flammable blend upon adding fairly large proportions in order to increase the volumetric refrigerating capacity while maintaining a favorable GWP.

For a non-flammable blend, on the other hand, a fairly large proportion of refrigerants with high fluor content (e.g. R125) must be added. A drawback here is the high GWP of more than approx. 900 for non-flammable R22/R407C alternatives and more than approx. 1300 with options for R404A/ R507A. Compared to R404A/ R507A, however, this means a reduction down to a third.

The future drastic "phase-down" of F-Gases, e.g. as part of the EU F-Gas Regulation, already leads to a demand for R404A/ R507A substitutes with GWP values clearly below 500. Although this is possible with an adequate composition of the blend (high proportions of HFO, R152a, possibly also hydrocarbons), the disadvantage will be its flammability (safety groups A2L or A2). In this case, the application will have higher safety requirements and will need an adequately adjusted system technology.

R410A currently has no non-flammable alternatives for a broader use in commercial applications. Either R32 (see page 23) as pure substance or blends of R32 and HFO can be used. Due to its high volumetric refrigerating capacity, this requires a very high proportion of R32, which is why only GWP values from approx. 400 to 500 can be achieved. With a higher HFO proportion, the GWP can be reduced even further, but at the cost of a clearly reduced refrigerating capacity.

All blend options described above with R1234yf and R1234ze(E) show a more or less distinct temperature glide due to boiling point differences of the individual components. The same criteria apply as described in context with R407C.

Beyond that, the discharge gas temperature of most R404A/R507A alternatives is considerably higher than for these HFC blends.

In single stage low temperature systems this may lead to restrictions in the compressor application range or require special measures for additional cooling. In transport applications or in low temperature systems with smaller condensing units, the compressors used can often not meet the required operating ranges, due to the high discharge gas temperatures. This is why refrigerant blends based on R32 and HFO with a higher proportion of R125 have also been developed. The GWP is slightly above 2000, but below the limit of 2500 set in the EU F-Gas Regulation from 2020. The main advantage of such blends is their moderate discharge gas temperature, which allows the operation within the typical application limits of R404A.

The following table (Tab. 4) shows the potential blend components for the alternatives described above. With some refrigerants the mixture components for R22/R407C and R404A/R507A substitutes are identical, but their distribution in percent is different.

In the meantime, Chemours, Honeywell, Arkema, Mexichem and Daikin Chemical have offered corresponding chemical variants for laboratory and field tests, and in some cases already for commercial use. A number of refrigerants are still declared as being under development and are only made available for testing purposes under special agreements. Until now, trade names are often used although a larger number of HFO/HFC blends are already listed in the ASHRAE nomenclature.

The following table (Tab. 5) lists a range of currently available refrigerants or refrigerants declared as development products. Due to the large number of different versions and the potential changes in development products, the tables on pages 42/43 (Tab. 7/8) only list data of alternatives for R134a, R404A/R507A and R410A which are already commercially available.

For testing the "Low GWP" refrigerants, AHRI (USA) has initiated the "Alternative Refrigerants Evaluation Program (AREP)". It has investigated and evaluated several of the products mentioned in Tab. 5 as well as halogen-free refrigerants.

Further development projects with "Low GWP" refrigerants

For specific applications, Chemours has developed a non-flammable (A1) R410A alternative, which is marketed in selected countries and regions under the trade name OpteonTM XP41 – listed by ASHRAE as R463A.

It is a mixture of R32, R125, R1234yf, R134a and CO_2 with a GWP of 1494. Despite the high proportion of R32 and R1234yf, flammability is suppressed by mixing with R125, R134a and CO_2.

Regarding thermodynamics, the differences to R410A are comparatively small. The addition of CO_2, however, leads to a distinct temperature glide, which may cause certain limitations for the application and places particular demand on the design of the heat exchangers.

All mixture components and their properties are well known, which means there are no additional particularities regarding material compatibility in comparison to the already known R410A alternatives.

The supply of compressors for laboratory or field tests requires an individual review of the specific application and a special agreement.

Some time ago, Honeywell has unveiled the new development of a non-flammable (A1) R410A alternative under the trade name Solstice® N-41 – listed by ASHRAE as R466A.

R466A is a mixture of R32, R125 and R13I1 (CF_3I – trifluoroiodomethane), an iodine-methane derivative not previously used in refrigeration. CF_3I is not flammable, as is R125, which means that the refrigerant is not flammable (A1), even with the relatively high proportion of R32 (A2L).

Despite the noticeable proportion of R125 with a GWP of 3500, the total GWP is 733 (AR4) and therefore in the range of R32 and R452B, which are however classified as A2L.

From a thermodynamic point of view, the differences between R410A and R466A are relatively small. Volumetric refrigerating capacity, pressure levels and discharge temperature are slightly higher, the refrigerant mass flow deviates slightly more (about 15 to 20% higher). The temperature glide is also very low.

Hence, R466A appears to be a promising substitute for R410A. However, due to the CF_3I share, there are still uncertainties regarding long-term chemical stability and material compatibility under the special requirements of the refrigeration cycle.

Further investigation is required, so a final assessment of R466A is currently not possible. In any case, as matters stand, this refrigerant cannot be used in state-of-the-art systems (retrofit). The supply of compressors for laboratory tests requires an individual review of the specific application as well as a special agreement.

AGC Chemicals propagates R1123 (CF_2=CHF) mixed with R32, partially with addition of R134yf, as an alternative to R410A and pure R32. It is an HCFO with very low ozone depletion potential (ODP). R1123 has a significantly higher volumetric refrigeration capacity than R1234yf or R1234ze(E) and is advantageous in this respect. However, the pressure level is even higher than of R32 and the critical temperature is only about 59°C. Apart from that, there are unanswered questions about the chemical long-term stability under the special requirements of the refrigeration cycle. According to the safety data sheet, this substance is also subject to very stringent safety requirements.

A final assessment of these mixtures is therefore currently not possible.

Comment from a compressor manufacturer's point of view:
It should be an aim to limit the product variety currently becoming apparent and to reduce the future supply to a few "standard refrigerants". It will not be possible for component and equipment manufacturers nor for installers and service companies to deal in practice with a larger range of alternatives.

BITZER was involved early on in various projects with HFO/HFC blends and was thus able to gain important insight into the use of these refrigerants. Semi-hermetic reciprocating compressors of the ECOLINE series as well as CS. and HS. screw compressors can already be used with this new generation of refrigerants.

Several of them have already been qualified and approved, the respective performance data is available on the BITZER SOFTWARE.

Scroll compressors of the ORBIT GSD6..VL and GSD8..VL series are approved and released for the use of the R32/HFO mixtures R452B and R454B.

Further information on the application of HFOs and HFO/HFC blends see brochure A-510, section 6.

09.20

Actual HFC Refrigerants	Alternatives		Components / Mixture components "Low GWP" alternatives (Examples)										
	Safety Group ↓	GWP④ ↓	**R1234yf A2L** GWP 4	**R1234ze(E) A2L** 7	**R32 A2L** 675	**R152a A2** 124	**R134a A1** 1430	**R125 A1** 3500	**R13I1⑤ A1** <1	**R227ea A1** 3220	**R1336mzz(E) A1** 7	**$CO_2$② A1** 1	**R290② A3** 3
R134a GWP 1430	A1	~ 600	✔	✔	✔		✔						
	A1	~ 300⑥		✔						✔			
	A1	< 150⑥		✔						✔	✔		
	A2L	< 150	✔	✔	✔	✔	✔						
	A2L	< 10	✔	✔									
R404A/R507A GWP 3922/3985	A1	< 2500①	✔		✔			✔					
	A1	~ 1400	✔	✔	✔		✔	✔					
	A2L	< 250	✔		✔	✔							
	A2L③	< 150	✔		✔							✔	
	A2	< 150	✔		✔								✔
R22/R407C GWP 1810/1774	A1	900..1400	✔	✔	✔		✔	✔					
	A2L	< 250	✔		✔	✔							
	A2L	< 150	✔		✔								
	A2	< 150	✔		✔								✔
R410A GWP 2088	A1	< 1500	✔		✔		✔	✔				✔	
	A1	< 750			✔			✔	✔				
	A2L	< 750			✔								
	A2L	~ 400..750	✔	✔	✔			✔					

① Refrigerating capacity, mass flow, discharge gas temperature similar to R404A
② Only low percentage – due to temperature glide (CO_2) and flammability (R290
② R32/HFO blends show lower refrigerating capacity than reference refrigerant, the addtion of CO_2 leads to high temperature glide
④ Approx. values according to IPCC IV (AR4)
⑤ R13I1 (CF_3I – tri-fluoroiodomethane) is an iodine-methane derivative
⑥ Lower volumetric refrigerating capacity than reference refrigerant

Tab. 4 Potential mixture components for "Low GWP" alternatives (examples)

09.20

Current HFC Refrigerants	„Low GWP" Alternatives for HFC refrigerant							
	ASHRAE Number	**Trade Name**		**Composition (with blends)**	**GWP③ AR4 (AR5)**	**Safety group**	**Boiling temperature [°C]④**	**Temperature glide [K]⑤**
R134a GWP 1430①	R450A	Solstice® N-13	Honeywell	R1234ze(E)/134a	604 (547)	A1	-24	0.6
	R456A	AC5X⑥	Koura (Mexichem)	R32/1234ze(E)/134a	687 (627)	A1	-30	4.8
	R513A	Opteon™ XP10 R513A	Chemours Daikin Chemical	R1234yf/134a	631 (573)	A1	-30	0
	R515B②	–	Honeywell	R1234ze(E)/227ea	293 (299)	A1	-19	0
	R471A②	–	Honeywell	R1234ze(E)/1336mzz(E)/227ea	148 (148)	A1	-17	3.2
	R1234yf	various		–	4 (< 1)	A2L	-30	0
	R1234ze(E)②	various		–	7 (< 1)	A2L	-19	0
	R444A	AC5⑥	Koura (Mexichem)	R32/152a/1234ze(E)	92 (89)	A2L	-34	10
	R516A	ARM-42	Arkema	R1234yf/R152a/R134a	142 (131)	A2L	-29	0
R404A/R507A GWP 3922/3985 **(R22/R407)**	R448A	Solstice® N-40	Honeywell	R32/125/1234yf/1234ze(E)/134a	1387 (1273)	A1	-46	6.2
	R449A	Opteon™ XP40 Forane® 449	Chemours Arkema	R32/125/1234yf/134a	1397 (1282)	A1	-46	5.7
	R452A	Opteon™ XP44	Chemours	R32/125/1234yf	2140 (1945)	A1	-47	3.8
	R454A	Opteon™ XL40 R454A	Chemours Daikin Chemical	R32/1234yf	239 (238)	A2L	-48	5.7
	R457B	ARM-20b	Arkema	R32/1234yf/152a	251 (251)	A2L	-47	6.1
	R454C②	Opteon™ XL20	Chemours	R32/1234yf	148 (146)	A2L	-46	7.8
	R455A	Solstice® L-40X	Honeywell	R32/1234yf/CO_2	148 (146)	A2L	-52	12.8
	R457A②	ARM-20a	Arkema	R32/1234yf/152a	139 (139)	A2L	-43	7.2
	R465A	ARM-25	Arkema	R32/1234yf/290	145 (143)	A2	-52	11.8
	R468A		Daikin Chemical	R32/1234yf/1132a	148 (147)	A2L	-51	12.3
R22/R407C GWP 1810/1774	R449C	Opteon™ XP20	Chemours	R32/125/1234yf/134a	1251 (1146)	A1	-44	6.1
R410A GWP 2088	R32	various		–	675 (677)	A2L	-52	0
	R452B	Opteon™ XL55 Solstice® L-41y	Chemours Honeywell	R32/125/1234yf	698 (676)	A2L	-51	0.9
	R454B	Opteon™ XL41	Chemours	R32/1234yf	466 (467)	A2L	-51	1.0
	R463A	Opteon™ XP41	Chemours	R32/125/1234yf/134a/CO_2	1494 (1377)	A1	-59	12.2
	R466A	Solstice® N-41	Honeywell	R32/125/13I1(CF_3I)	733 (696)	A1	-52	0.7

① The relatively low GWP allows the use of R134a also on longer term.
② Lower volumetric refrigerating capacity than reference refrigerant
③ AR4: according to IPCC IV // AR5: according to IPCC V – time horizon 100 years
④ Rounded values
⑤ Total glide from bubble to dew line at 1.013 bar (abs.)
⑥ Development product

Tab. 5 „Low GWP" alternatives for HFC refrigerants – for further data see Tab. 7 and 8 („Refrigerant Properties")

NH_3 (Ammonia) as alternative refrigerant

The refrigerant NH_3 has been used for more than a century in industrial and larger refrigeration plants. It has no ozone depletion potential and no direct global warming potential. The efficiency is at least as good as that of R22, in some areas even more favourable; the contribution to the indirect global warming effect is therefore small. In addition, its price is exceptionally low. Is it therefore an ideal refrigerant and an optimum substitute for R22 or an alternative for HFCs!? NH_3 has indeed very positive features, which can be exploited quite well in large refrigeration systems and heat pumps.

Unfortunately there are also negative aspects, which restrict the wider use in the commercial area or require costly and sometimes new technical developments.

A disadvantage with NH_3 is the high isentropic exponent (NH_3 = 1.31 / R22 = 1.19 / R134a = 1.1), which results in a discharge temperature even significantly higher than that of R22. Single stage compression is therefore already subject to certain restrictions below an evaporating temperature of around -10°C.

The question of suitable lubricants is also not satisfactorily solved for smaller plants in some kinds of applications. The most commonly used mineral oils and polyalpha-olefins are not soluble with the refrigerant. They must be separated with complex technology and seriously limit the use of "direct expansion evaporators" due to the deterioration in the heat transfer.

Special demands are made on the thermal stability of the lubricants due to the high discharge gas temperatures. This is especially valid when automatic operation is considered where the oil is supposed to remain in the circuit for years without losing any of its stability.
NH_3 has an extraordinarily high enthalpy difference and thus a very small circulating mass flow (approximately 13 to 15% compared to R22). This feature, which is favourable for large plants, makes the control of the refrigerant injection more difficult with small capacities.

Further to be considered is the corrosive action on copper containing materials; pipe lines must therefore be made of steel. This also hinders the development of motor windings resistant to NH_3 as basis for semi-hermetic constructions. Another difficulty arises from the electrical conductivity of the refrigerant in case of higher moisture content.

Additional characteristics include toxicity and flammability, which require special safety measures for the construction and operation of such systems.

Resulting design and construction criteria

Based on the present "state of technology", industrial NH_3 systems demand a completely different plant technology, compared to usual commercial systems.

Due to the insolubility with the lubricating oil and the specific characteristics of the refrigerant, high efficiency oil separators and flooded evaporators with gravity or pump circulation are usually employed. Because of the danger to the public and to the product to be cooled, the evaporator often cannot be installed directly at the cold space and the heat must be transported by a secondary refrigerant circuit.

Due to the thermal behaviour, two stage compressors or screw compressors with generously sized oil coolers must be used even at medium pressure ratios.

Refrigerant lines, heat exchangers and fittings must be made of steel; larger size pipe lines must be examined by a certified inspector. In some cases, aluminium can also be used as a material.

Depending upon the size of the plant and the refrigerant charge, corresponding safety measures and special machine rooms are required.

The refrigeration compressor is usually of "open" design, the drive motor is a separate component.

These measures significantly increase the expenditure for NH_3 plants, especially for medium and smaller capacities.

Efforts are therefore being made world-wide to develop simpler systems which can also be used in the commercial area.

A part of the research programs is dealing with part soluble lubricants, with the aim of improving oil circulation in the system. Simplified methods for automatic return of non-soluble oils are also being examined as an alternative.

BITZER is strongly involved in these projects and has a large number of operating compressors. The experiences up to now have revealed that systems with partly soluble oils are difficult to manage. The moisture content in the system has an important influence on the chemical stability of the circuit and the wear of the compressor. Besides, high refrigerant solution in the oil (wet operation, insufficient oil temperature) leads to strong wear on the bearings and other moving parts. This is due to the enormous volume change when NH_3 evaporates in the lubricated areas.
These research developments are being continued, with focus also on alternative solutions for non-soluble lubricants.

Various equipment manufacturers have developed special evaporators, allowing significantly reduced refrigerant charge. There is a strong trend towards so-called "low charge" systems, i.a. with regard to safety requirements, which are also largely determined by the refrigerant charge.

In addition to this, there are developments for the "sealing" of NH_3 plants: compact liquid chillers (charge below 50 kg), installed in a closed container and partly with an integrated water reservoir to absorb NH_3 in case of a leak. This type of compact unit can be installed in areas which were previously reserved for plants with refrigerants of safety group A1 due to safety requirements.

An assessment of NH_3 compact systems – instead of systems using HFC refrigerants and conventional technology – is only possible on an individual basis, taking into account the particular application. From a merely technical viewpoint and presupposing an acceptable price level, a wider range of products will supposedly become available in the foreseeable future.

The product range from BITZER today includes an extensive selection of optimized NH_3 compressors for various types of lubricants:

- **Single stage open reciprocating compressors (displacement 19 to 152 m^3/h with 1450 rpm) for air conditioning, medium temperature and booster applications**
- **Open screw compressors (displacement 84 to 1015 m^3/h – with parallel operation to 4060 m^3/h – with 2900 rpm) for air conditioning, medium and low temperature cooling.**
  Options for low temperature cooling:
  – Single stage operation
  – Economiser operation
  – Booster operation

Conversion of existing plants

The refrigerant NH_3 is not suitable for the conversion of existing (H)CFC or HFC plants; they must be constructed completely new with all components.

Supplementary BITZER information concerning the application of NH_3 (see also https://www.bitzer.de)

- **Technical Information AT-640 "Use of Ammonia (R717) in BITZER compressors"**

R723 (NH_3/DME) as an alternative to NH_3

The previously described experiences with the use of NH_3 in commercial refrigeration plants with direct evaporation caused further experiments on the basis of NH_3 by adding an oil soluble refrigerant component. Main goals were improved oil transport and heat transmission with conventional lubricants, along with a reduced discharge gas temperature for the extended application range with single stage compressors.

The result of this research project is a refrigerant blend of NH_3 (60%) and dimethyl ether "DME" (40%), It was developed by the Institute of Air Handling and Refrigeration (ILK) in Dresden, Germany, and has been applied in a series of real systems. As a largely inorganic refrigerant it received the designation R723 due to it its average molecular weight of 23 kg/kmol in accordance to the standard refrigerant nomenclature.

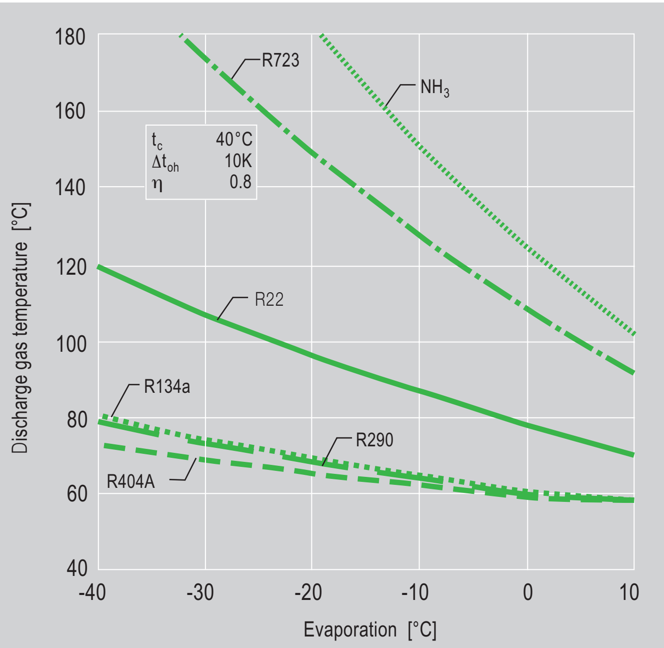


Fig. 24 Comparison of discharge gas temperatures

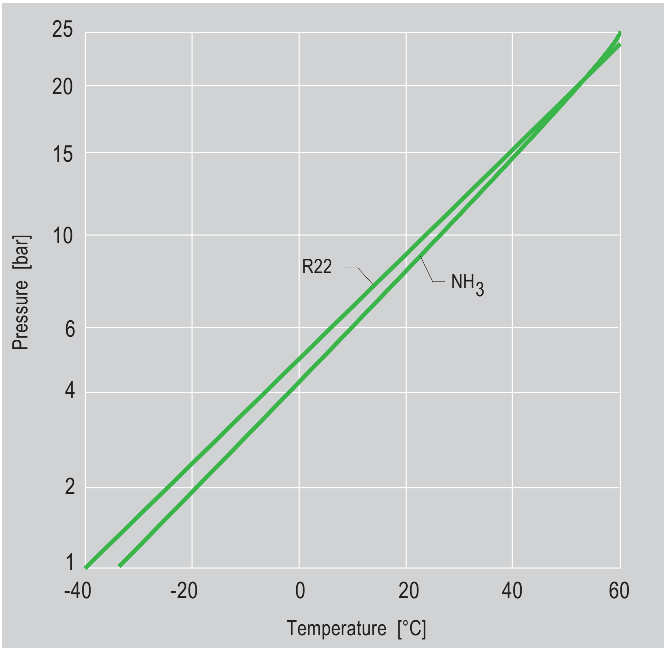


Fig. 25 NH_3/R22 – comparison of pressure levels

DME was selected as an additional component for its good solubility and high individual stability. Its boiling point is -26°C, the adiabatic exponent is relatively low, it is not toxic and available in high purity. In the abovementioned concentration NH_3 and DME form an azeotropic blend characterised by a slightly higher pressure level than pure NH_3. The boiling point lies at -36.5°C (NH_3 -33.4°C), 26 bar (abs.) of condensing pressure corresponds to 58.2°C (NH_3 59.7°C).

The discharge gas temperature in air conditioning and medium temperature ranges decreases by about 10 to 25 K (Fig. 24) and allows an extended application range to higher pressure ratios. Thermodynamic calculations conclude a single-digit percent rise in refrigerating capacity compared to NH_3. The coefficient of performance is similar and is even more favourable at high pressure ratios, confirmed by experiments. Due to the lower temperature level during compression, an improved volumetric and isentropic efficiency can be expected, at least with reciprocating compressors in case of an increasing pressure ratio.

Due to the higher molecular weight of DME, mass flow and vapour density increase by nearly 50% compared to NH_3, although this is of little importance to commercial plants, especially in short circuits. In conventional industrial refrigeration plants, however, this is a substantial criterion with regard to pressure drops and refrigerant circulation. These considerations again show that the preferred application area of R723 is in commercial applications and especially in liquid chillers.

Material compatibility is comparable to that of NH_3. Although non-ferrous metals (e.g. CuNi alloys, bronze, hard solders) are potentially suitable, provided minimum water content in the system (< 1000 ppm), a system design similar to typical ammonia practise is recommended.

Mineral oils or (preferred) polyalpha olefin are suitable lubricants. As mentioned before, the proportion of DME leads to improved oil solubility and a partial miscibility. Furthermore, the relatively low liquid density and an increased DME concentration in the oil enhances oil circulation. PAG oils would be fully or partly miscible with R723 for typical applications, but are not recommended because of the chemical stability and high solubility in the compressor crankcase (strong vapour development in the bearings).

Tests have shown that the heat transfer coefficient at evaporation and high heat flux is improved in systems with R723 and mineral oil compared to NH_3 with mineral oil.

Further characteristics are toxicity and flammability. The DME content lowers the ignition point in air from 15 to 6%. However, the azeotrope is ranked in safety group B2, but may receive a different classification in case of a revised assessment.

Resulting layout criteria

Experiences with the NH_3 compact systems described above can be used in plant technology. However, the component layout has to be adjusted considering the higher mass flow. By appropriate selection of the evaporator and the expansion valve, a very stable superheat control must be ensured. Due to the improved oil solubility, „wet operation" can have considerable negative results compared to NH_3 systems with non-soluble oil.

With regard to safety regulations, the same criteria apply to installation and operation as for NH_3 plants.

Suitable compressors are special NH_3 versions which possibly have to be adapted to the mass flow and the continuous oil circulation. An oil separator is usually not necessary with reciprocating compressors.

BITZER NH_3 reciprocating compressors are suitable for R723 in principle. An individual selection of specifically adapted compressors is possible on demand.

R290 (Propane) as alternative refrigerant

R290 (propane) can also be used as a substitute refrigerant. Being an organic compound (hydrocarbon), it has no ozone depletion potential and a negligible direct global warming effect. To take into consideration however, is a certain contribution to summer smog.

Pressure levels and refrigerating capacity are similar to R22, and its temperature behaviour is as favourable as with R134a.

There are no particular problems with material. In contrast to NH_3, copper materials are also suitable, so that semi-hermetic and hermetic compressors are possible. Common mineral oils of HCFC systems can be used here as a lubricant over a wide application range. Polyol esters (POE) and polyalpha-olefins (PAO) offer even more favorable properties.

Refrigeration plants with R290 have been in operation world-wide for many years, mainly in the industrial area – it is a "proven" refrigerant.
Meanwhile R290 is also used in smaller compact systems with low refrigerant charges like residential air-conditioning units and heat pumps. Furthermore, a rising trend can be observed in its use with commercial refrigeration systems and chillers.

Propane is offered also as a mixture with Isobutane (R600a) or Ethan (R170), in order to provide a similar performance to halocarbon refrigerants. Pure Isobutane is mostly intended as a substitute for R12 in small systems (preferably domestic refrigerators and freezers).

The disadvantage of hydrocarbons is their high flammability, therefore they are classified as refrigerants of "Safety Group A3". Based on the refrigerant charge quantities commonly used in commercial systems, the system design and risk analysis must be in accordance with explosion protection regulations.

Semi-hermetic compressors in so-called "hermetically sealed" systems are in this case subject to regulations for hazardous zone 2 (only seldom and short term risk). Safety demands include special devices to protect against excess pressures and special arrangements for the electrical system. In addition, measures are required to ensure hazard free ventilation to effectively prevent a flammable gas mixture in case of refrigerant leakage.

Design requirements are defined by standards (e.g. EN378) and may vary in different countries. For systems applied in the EU, an assessment according to EC Directive 94/9/EC (ATEX) may become necessary as well. With open compressors, this will possibly lead to a classification in zone 1 – which demands, however, electrical equipment in special flame-proof design.

Resulting design criteria

Apart from the measures mentioned above, propane systems require practically no special features in the medium and low temperature ranges compared to a usual (H)CFC and HFC system. When sizing components, however, the relatively low mass flow should be considered (approximately 55 to 60% compared to R22). An advantage here is that the refrigerant charge can be greatly reduced. From the thermodynamic point of view, an internal heat exchanger between the suction and liquid line is recommended as this will improve the refrigerating capacity and COP.

Owing to the particularly high solubility of R290 (and R1270) in common lubricants, BITZER R290/R1270 compressors are charged with special oil of a high viscosity index and particularly good tribological properties.
Again, an internal heat exchanger is of advantage as it leads to higher oil temperatures, lower solubility and therefore improved viscosity.

Due to the very favourable temperature behaviour (Fig. 24), single stage compressors can be used down to approximately - 40°C evaporation temperature. R290 could thus also be considered as an alternative for some of the HFC blends.

A range of ECOLINE compressors and CS. compact screws is available for R290. Due to the individual requirements a specifically equipped compressor version is offered. Inquiries and orders need a clear reference to R290. The handling of the order includes an individual agreement between the contract partners. Open reciprocating compressors are also available for R290, together with a comprehensive program of flame-proof accessories which may be required.

Conversion of existing plants with R22 or HFC to R290

Due to the special safety measures when using R290, a conversion of existing systems only seems possible in exceptional cases. They are limited to systems, which can be modified to meet the corresponding safety regulations with an acceptable effort.

Supplementary BITZER information concerning the use of R290 (see also https://www.bitzer.de)

- **Technical Information AT-660 “Use of propane (R290) and propene (R1270) in semi-hermetic BITZER compressors”**

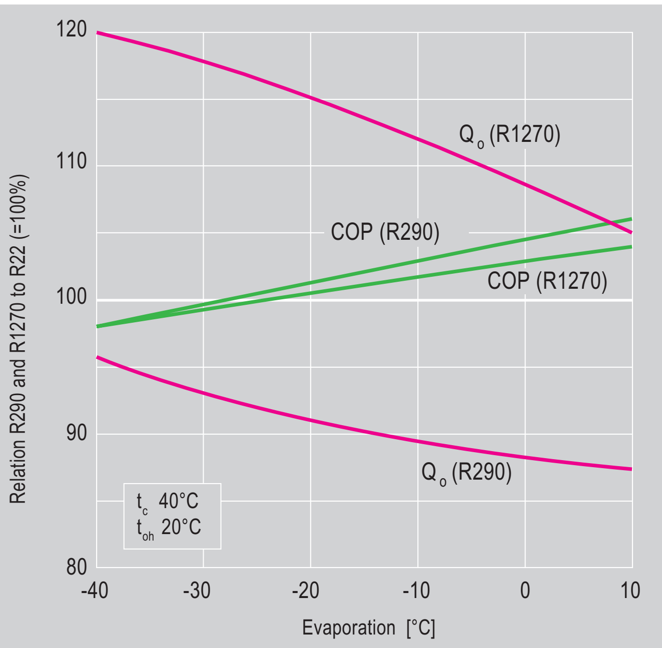


Fig. 26 R290/R1270/R22 – comparison of performance data of a semi-hermetic compressor

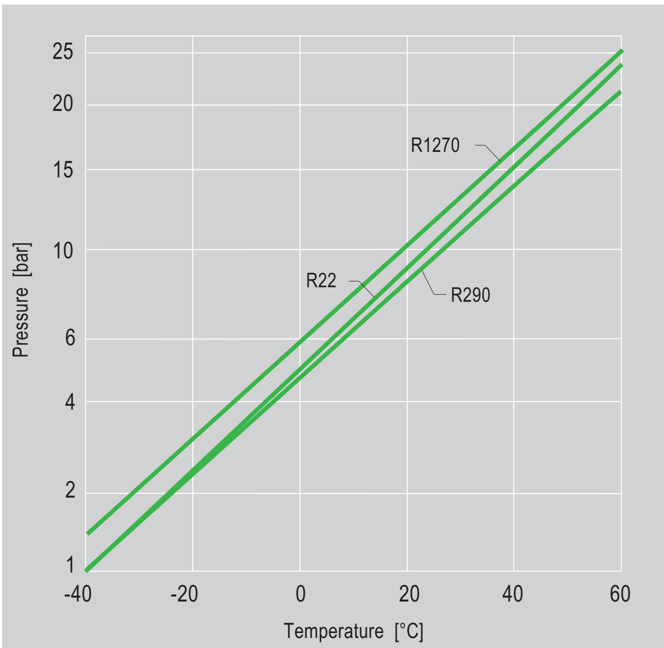


Fig. 27 R290/R1270/R22 – comparison of pressure levels

Propylene (R1270) as an alternative to Propane

For some time there has been increasing interest in using propylene (propene) as a substitute for R22 or HFC. Due to its higher volumetric refrigerating capacity and lower boiling temperature (compared to R290), applications in medium and low temperature systems are of particular interest, e.g. liquid chillers for supermarkets. On the other hand, higher pressure levels (> 20%) and discharge gas temperatures have to be taken into consideration, thus restricting the possible application range.

Material compatibility is comparable to propane, as is the choice of lubricants. Propylene is also easily inflammable and belongs to the safety group A3. The same safety regulations are therefore to be observed as with propane (page 31).

Due to the chemical double bond, propylene reacts quite easily, risking polymerization at high pressure and temperature levels. However, tests by hydrocarbon manufacturers and stability tests in real applications show practically no reactivity in refrigeration systems. Doubts have occasionally been voiced in some literature regarding possible carcinogenic effects of propylene. These assumptions have been disproved by appropriate studies.

Resulting design criteria

With regard to system technology, experience gained from the use of propane can widely be applied to propylene. However, component dimensions have to be altered due to higher volumetric refrigerating capacity (Fig. 26). The compressor displacement is correspondingly lower, as are the suction and high pressure volume flows. Because of higher vapour density, the mass flow is almost the same as for R290. As liquid density is nearly identical, the same applies to the liquid volume in circulation.

As with R290, an internal heat exchanger between suction and liquid lines is of advantage. However, due to the higher discharge gas temperature of R1270, restrictions are partly necessary at high pressure ratios.

A range of ECOLINE compressors and CS. compact screws is available for R1270. Due to the individual requirements a specifically equipped compressor version is offered. Inquiries and orders need a clear reference to R1270.

The handling of the order includes an individual agreement between the contract partners. Open reciprocating compressors are also available for R1270, together with a comprehensive program of flame-proof accessories which may be required.

Supplementary BITZER information concerning the use of R1270 (see also https://www.bitzer.de)

- ❏ **Technical Information AT-660 “Use of propane (R290) and propene (R1270) in semi-hermetic BITZER compressors”**

Carbon dioxide R744 (CO_2) as an alternative refrigerant and secondary fluid

CO_2 has had a long tradition in the refrigeration technology reaching far into the 19th century. It has no ozone depleting potential, a negligible direct global warming potential (GWP = 1), is chemically inactive, non-flammable and not toxic in the classical sense. Therefore, CO_2 is not subjected to the stringent containment demands of HFCs (F-Gas Regulation) and flammable or toxic refrigerants. However, compared to HFCs the lower critical value in air has to be considered. For closed rooms, this may require special safety and detection systems.

CO_2 is also low in cost and there is no necessity for recovery and disposal. In addition, it has a very high volumetric refrigerating capacity: depending on operating conditions, approx. 5 to 8 times as high as R22 and NH_3.

Above all, the safety relevant characteristics were an essential reason for the initial widespread use. The main focus for applications were e.g. marine refrigeration systems. With the introduction of the "(H)CFC Safety Refrigerants", CO_2 became less popular and had nearly disappeared by the 1950's.

The main reasons for that are its relatively unfavourable thermodynamic characteristics for usual applications in refrigeration and air conditioning.

The discharge pressure with CO_2 is extremely high, and the critical temperature at 31°C (74 bar) very low. Depending on the heat sink temperature at the high pressure side, transcritical operations with pressures beyond 100 bar are required. Under these conditions, energy efficiency is often lower than in the classic vapour compression process (with condensation), therefore the indirect global warming effect is higher.

Nonetheless, there is a range of applications in which CO_2 can be used very economically and with favourable eco-efficiency. These include subcritical cascade plants, but also transcritical systems, in which the temperature glide on the high pressure side can be used advantageously, or the system conditions permit subcritical operation for long periods. It should further be noted that the heat transfer coefficients of CO_2 are considerably higher than of other refrigerants – with the potential of very low temperature differences in evaporators, condensers, and gas coolers. Moreover, the necessary pipe dimensions are very small, and the influence of the pressure drop is comparably low. In addition, when used as a secondary fluid, the energy demand for circulation pumps is extremely low.

In the following section, a few examples of subcritical systems and resulting design criteria are described. An additional section provides details on transcritical applications.

Subcritical CO_2 applications

From energy and pressure level points of view, very beneficial applications can be seen for industrial and larger commercial refrigeration plants. For this, CO_2 can be used as a secondary fluid in a cascade system and if required, in combination with a further booster stage for lower evaporating temperatures (Fig. 30).

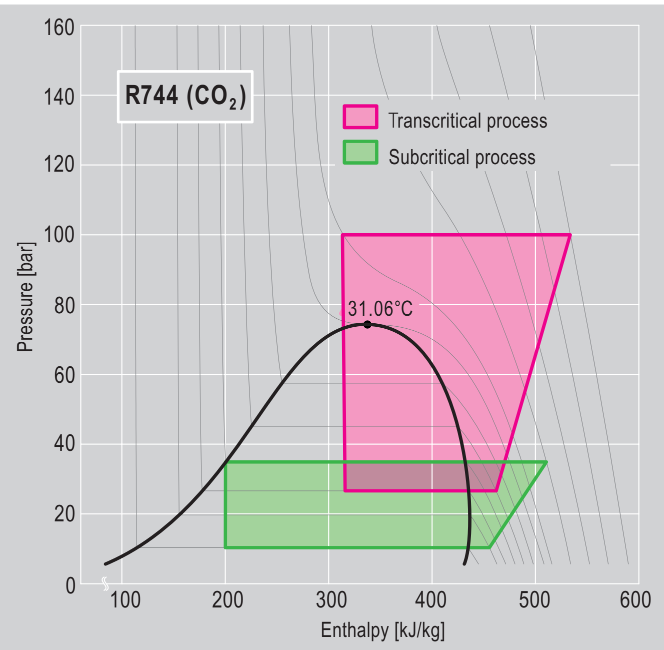


Fig. 28 R744(CO_2) – pressure/enthalpy diagram

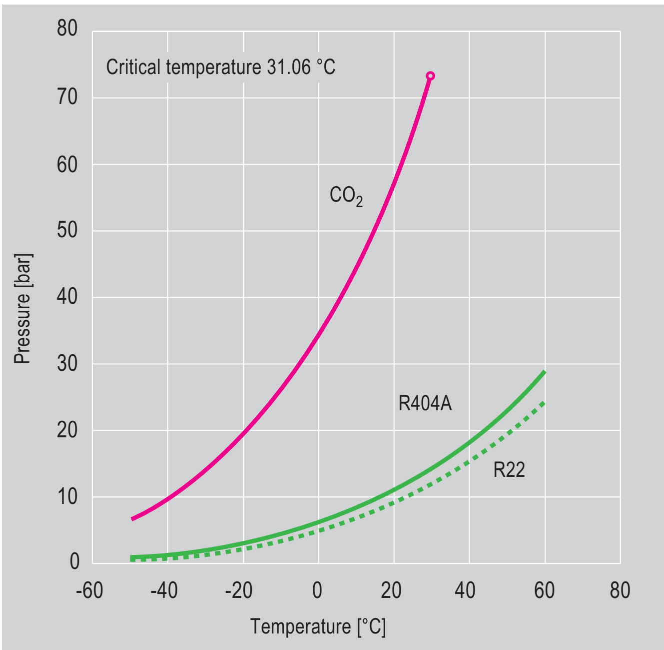


Fig. 29 R744(CO_2)/R22/R404A – comparison of pressure levels

The operating conditions are always subcritical which guarantees good efficiency levels. In the most favourable application range (approx. -10 to -50°C), pressures are still on a level where already available components, e.g. for R410A, can be matched with acceptable effort.

Resulting design criteria

For the high temperature side of such a cascade system, a compact cooling unit can be used, whose evaporator serves on the secondary side as the condenser for CO_2. Chlorine-free refrigerants are suitable, e.g. NH_3, HCs or HFCs, HFO and HFO/HFC blends.

With NH_3, the cascade heat exchanger should be designed in a way that the dreaded build-up of ammonium carbonate in the case of leakage is prevented. This technology has been applied in breweries for a long time.

A secondary circuit for larger plants with CO_2 could be constructed utilising, to a wide extent, the same principles for a low pressure pump circulating system, as is often used with NH_3 plants. The essential difference is the condensing of CO_2 in the cascade cooler, while the receiver tank (accumulator) only serves as a supply vessel.

The extremely high volumetric refrigerating capacity of CO_2 (latent heat through the changing of phases) leads to very low mass flow rates, allows for small cross sectional pipe and minimal energy needs for the circulating pumps.

There are different solutions for the combination with a further compression stage, e.g. for low temperatures.

Fig. 30 shows a variation with an additional receiver, which one or more booster compressors will bring down to the necessary evaporation pressure. Likewise, the discharge gas is fed into the cascade cooler, condenses and is carried over to the receiver. The feeding of the low pressure receiver (LT) is achieved by a level control device.

Instead of conventional pump circulation the booster stage can also be built as a so-called LPR system.The circulation pump is thus not necessary, but the number of evaporators is then limited with view to an even distribution of the injected CO_2.

In the case of a system breakdown where a high rise in pressure could occur, safety valves can vent the CO_2 to the atmosphere with the necessary precautions. As an alternative, additional cooling units for CO_2 condensation are also used where longer shut-off periods can be bridged without a critical pressure increase.

For systems in commercial applications, a direct expansion version is possible as well.

Supermarket plants with their usually widely branched pipe work offer an especially good potential in this regard: The medium temperature system is carried out in a conventional design or with a secondary circuit, for low temperature application combined with a CO_2 cascade system (for subcritical operation). A system example is shown in Fig. 31.

For a general application, however, not all requirements can be met at the moment. It is worth considering that system technology changes in many respects and specially adjusted components are necessary to meet the demands.

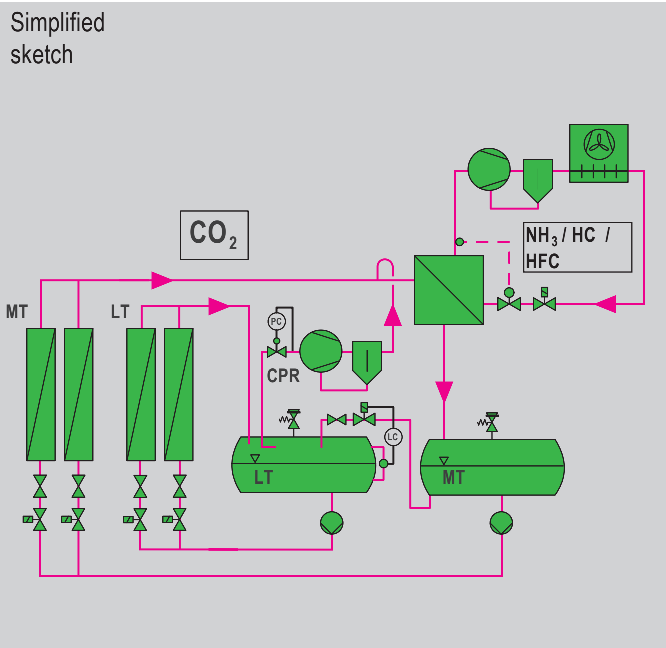


Fig. 30 Casacde system with CO_2 for industrial applications

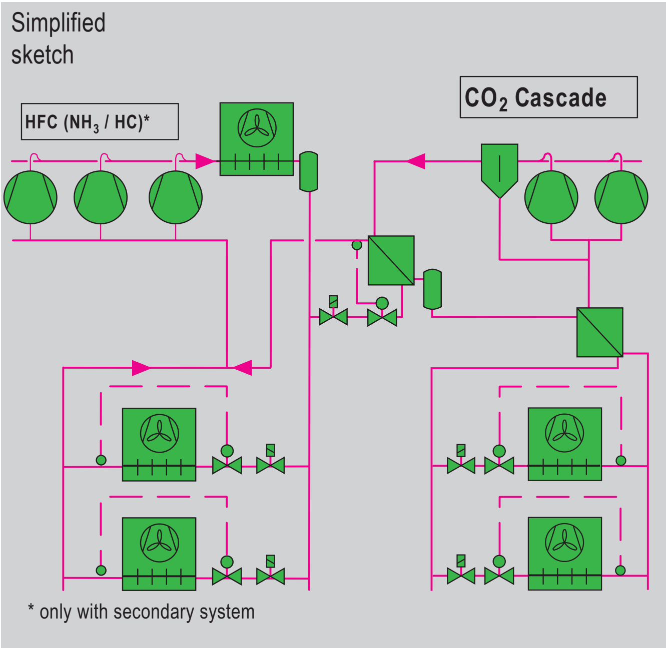


Fig. 31 Conventional refrigeration system combined with CO_2 low temperature cascade

The compressors, for example, must be properly designed because of the high vapour density and pressure levels (particularly on the suction side). There are also specific requirements with regard to materials. Furthermore only highly dehydrated CO_2 must be used.

High demands are made on lubricants as well. Conventional oils are mostly not miscible and therefore require costly measures to return the oil from the system. On the other hand, if miscible and highly soluble POE are used, the viscosity is strongly reduced. Further information to lubricants see page 41 and Fig. 37, page 45.

For subcritical CO_2 applications BITZER offers two series of special compressors.

Supplementary BITZER information concerning compressor selection for subcritical CO_2 systems
(see also https://www.bitzer.de)

- ❑ **Brochure KP-120**
  Semi-hermetic reciprocating compressors for subcritical CO_2 applications (LP/HP standstill pressures up to 30/53 bar)
- ❑ **Brochure KP-122**
  Semi-hermetic reciprocating compressors for subcritical CO_2 applications (LP/HP standstill pressures up to 100 bar)
- ❑ **Additional publications upon request**

Transcritical CO_2 applications

Transcritical processes are characterized in that the heat rejection on the high pressure side proceeds isobar but not isotherm. Contrary to the condensation process during subcritical operation, gas cooling (desuperheating) occurs, with corresponding temperature glide. Therefore, the heat exchanger is described as gas cooler. As long as operation remains above the critical pressure (74 bar), only high-density vapour will be transported. Condensation only takes place after expansion to a lower pressure level – e.g. by interstage expansion in an intermediate pressure receiver. Depending on the temperature curve of the heat sink, a system designed for transcritical operation can also be operated subcritically – with higher efficiency. In this case, the gas cooler becomes the condenser.

Another feature of transcritical operation is the necessary control of the high pressure to a defined level. This "optimum pressure" is determined as a function of gas cooler outlet temperature by means of balancing between the highest possible enthalpy difference and at once minimum compression work. It must be adapted to the relevant operating conditions using an intelligent modulating controller (see system example, Fig. 32).

As described before, under purely thermodynamic aspects, the transcritical operating mode appears to be unfavourable in terms of energy efficiency. In fact, this is true for systems with a fairly high temperature level of the heat sink on the high pressure side. However, additional measures can improve efficiency, such as the use of parallel compression (economiser system) and/or ejectors or expanders for recovering the throttling losses during expansion of the refrigerant.

Apart from that, there are application areas in which a transcritical process is advantageous in energy demand. These include heat pumps for sanitary water or drying processes. With the usually very high temperature gradients between the discharge temperature at the gas cooler intake and the heat sink intake temperature, a very low gas temperature outlet is achievable. This is facilitated by the temperature glide curve and the relatively high mean temperature difference between CO_2 vapour and secondary fluid. The low gas outlet temperature leads to a particularly high enthalpy difference, and therefore to a high system COP.

Low-capacity sanitary water heat pumps are already manufactured and used in large quantities. Plants for medium to higher capacities (e.g. hotels, swimming pools, drying systems) must be planned and realised individually. Their number is therefore still limited, but with an upward trend. Apart from these specific applications, there is also a range of developments for the classical areas of refrigeration and air-conditioning, e.g. supermarket refrigeration. Installations with parallel compounded compressors are in operation to a larger scale. They are predominantly booster systems where medium and low temperature circuits are connected (without heat exchanger). The operating experience and the calculated energy costs show promising results. However, the investment costs are still higher than for conventional plants with HFCs and direct expansion.

On the one hand, the favourable energy costs are due to the high degree of optimized components and the system control, as well as the previously described advantages regarding heat transfer and pressure drop. On the other hand, these installations are preferably used in climate zones permitting very high running times in subcritical operation due to the annual ambient temperature profile.

For increasing the efficiency of CO_2 supermarket systems and for using them in warmer climate zones, the technologies described above using parallel compression and/or ejectors are increasingly used.

Therefore, but also because of very demanding technology and requirements for qualification of planners and service personnel, CO_2 technology cannot be regarded as a general replacement for plants using HFC refrigerants.

Resulting design criteria

Detailed information on this topic would go beyond the scope of this publication. In any case, the system and control techniques are substantially different from conventional plants. Already when considering pressure levels as well as volume and mass flow ratios specially developed components, controls, and safety devices as well as suitably dimensioned pipework must be provided.

The compressor technology is particularly demanding. The special requirements result in a completely independent approach. For example, this involves design, materials (bursting resistance), displacement, crank gear, working valves, lubrication system, as well as compressor and motor cooling. Hereby, the high thermal load severely limits the application for single-stage compression. Low temperature cooling requires 2-stage operation, whereby separate high and low pressure compressors are particularly advantageous with parallel compounded systems.

The criteria mentioned above in connection with subcritical systems apply to an even higher degree for lubricants. For further information to lubricants see page 41 and Fig. 37, page 45.

Further development is necessary in various areas, and transcritical CO_2 technology cannot in general be regarded as state-of-the-art.

For transcritical CO_2 applications, BITZER offers a wide range of special compressors. Their use is aimed at specific applications, therefore individual examination and assessment are required.

Suplementary BITZER information concerning compressor selection for transcritical CO_2 systems (see also https://www.bitzer.de)

- ❑ **Brochure KP-130 Semi-hermetic reciprocating compressors for transcritical CO_2 applications**
- ❑ **Additional publications upon request**

CO_2 in mobile air-conditioning systems

Within the scope of the long-discussed measures for reducing direct refrigerant emissions, and the ban on the use of R134a in MAC systems within the EU, the development of CO_2 systems has been pursued intensively since several years.

At first glance, efficiency and therefore indirect emissions from CO_2 systems under typical ambient conditions appear to be unfavourable. But it must be considered that previous R134a systems are less efficient than stationary plants of the same capacity, because of specific installation conditions and high pressure losses in pipework and heat exchangers. With CO_2, pressure losses have significantly less influence. Moreover, system efficiency is further improved by the high heat transfer coefficients in the heat exchangers.

This is why optimized CO_2 air conditioning systems are able to achieve efficiencies comparable to those of R134a. Regarding the usual leakage rates of such systems, a more favourable balance is obtained in terms of TEWI.

From today's viewpoint, it is not yet possible to make a prediction as to whether CO_2 can in the long run prevail in this application. It certainly also depends on the experience with "low GWP" refrigerants that have meanwhile been introduced by the automotive industry (see chapter R1234yf, page 11). Among others, operating safety, costs, and global logistics will play an important role.

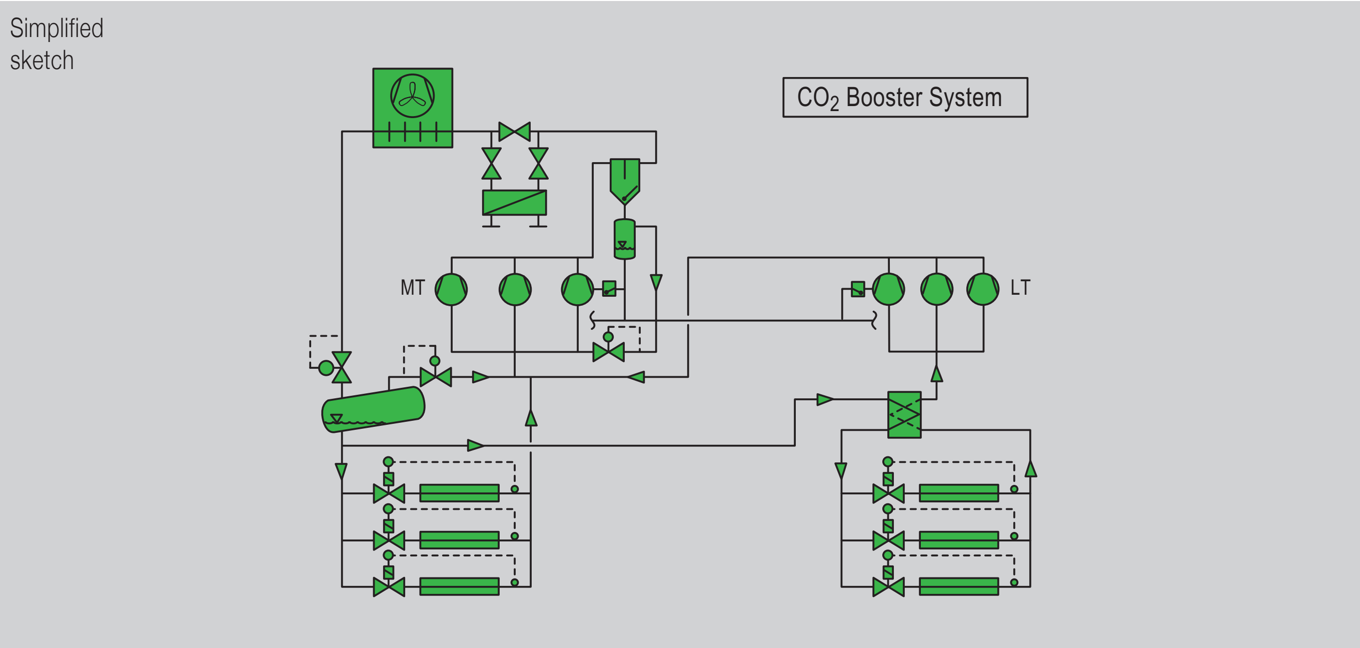


Fig. 32 Example of a transcritical CO_2 Booster system

R124 and R142b as substitutes for R114 and R12B1

In place of R114 and R12B1 previously used in high-temperature heat pumps and crane air conditioning systems, HCFCs R124 and R142b can still be used as alternatives in most regions outside of the EU.

With these gases it is also possible to use long proven lubricants, preferably mineral oils and alkyl benzenes with high viscosity.

Because of their ozone depleting potential, these refrigerants will only be an interim solution. In the EU member states as well as in some other regions, the application of HCFCs is no longer allowed. For R124 and R142b the same restrictions are valid as for R22 (page 8). The flammability of R142b and the resulting safety implications should also be considered (safety group A2).

Resulting design criteria/ Converting existing plants

Compared to R114, the alternatives have lower boiling temperatures (approx. -10°C), which results in larger differences in the pressure levels and volumetric refrigerating capacities. This leads to stronger limitations in the application range at high evaporating and condensing temperatures.

Converting an existing installation will in most cases necessitate the exchange of the compressor and control devices. Owing to the lower volume flow (higher volumetric refrigerating capacity), adjustments to the evaporator and the suction line may be required.

Over the previous years BITZER compressors have been found to be well suited with R124 and R142b in actual installations. Depending on the application range and compressor type modifications are necessary, however. Performance data including further design instructions are available on request.

Chlorine free substitutes for special applications

Due to the limited market for systems with extra high and low temperature applications, the development of alternative refrigerants and system components for these has been pursued less intensely.

In the meantime, a group of alternatives for the CFC R114 and Halon R12B1 (high temperature), R13B1, R13 and R503 (extra low temperature) have been offered as replacements. On closer examination, however, the thermodynamic properties of the alternatives differ considerably from the previously used substances. This can cause costly changes especially with the conversion of existing systems.

Alternatives for R114 and R12B1

R227ea and R236fa are considered suitable substitutes even though they may no longer be used in new installations in the EU from 2020, due to their high GWP.

R227ea cannot be seen as a full replacement. Although tests and experience in real plants show favorable results, a critical temperature of 102°C limits the condensing temperature to 85..90°C with conventional plant technology.

R236fa provides the more favourable conditions at least in this regard – the critical temperature is above 120°C. A disadvantage, however, is the lower volumetric refrigerating capacity. It is similar to R114 and 40% below the performance of R124, which is still widely used for extra high temperature applications.

R600a (Isobutane) will be an interesting alternative where safety regulations allow the use of hydrocarbons (safety group A3). With a critical temperature of 135°C, condensing temperatures of 100°C and more are within reach. The volumetric refrigerating capacity is almost identical to R124.

The "Low GWP" refrigerant R1234ze(E) (page 24) can also be regarded as a potential candidate for extra high temperature applications. Compared to R124, its refrigerating capacity is 10 to 20% higher, its pressure level about 25% higher. At identical refrigerating capacities, the mass flow differs only slightly. Its critical temperature is 109°C, which would enable an economical operation up to a condensing temperature of about 90°C. However, like R1234yf, R1234ze(E) shows low flammability and therefore classified into the new safety group A2L. The corresponding safety regulations must be observed.

As no sufficient operating experience is available so far, the suitability of this refrigerant for long-term use cannot be assessed yet.

For high temperature heat pumps in process technology and special applications at high temperatures, the low pressure refrigerants based on HFO and HCFO developed primarily for systems with turbo compressors are also potentially suitable (page 24).

They are characterised by very high critical temperatures (> 130°C), which enable economical operation at condensing temperatures of sometimes well above 100°C. However, only purpose-built compressors and system components can be used here.

Another advantage is their very low GWP and the classification in safety group A1 (non-flammable, non-toxic).

A detailed evaluation of these refrigerants is not yet possible with respect to the chemical stability of the refrigerants and of the lubricants at the very high operating temperatures and the long service life required for industrial systems.

Special applications also include cogeneration systems – "Organic Rankine Cycle" (ORC), which become increasingly important. In addition to the potentially suitable substances listed in the table above, a series of other fluids are possible, depending on the temperature level of the heat source and heat sink.

They include the so far mostly used R245fa (GWP 1050) with a critical temperature of 154°C and a boiling temperature of 15.1°C.

Solvay offers further refrigerants for ORC applications, containing the base component R365mfc. A product with the trade name Solkatherm® SES36 already presented several years ago contains perfluoropolyether as a blend component. It is an azeotropic blend with a critical temperature of 178°C. Meanwhile two zeotropic blends containing R365mfc and R227ea have been developed whose critical temperatures are 177°C and 182°C, due to different mixing ratios. They are available under the trade names Solkatherm® SES24 and SES30.
In ORC systems zeotropic behavior may be advantageous. In the case of single-phase heat sources and heat sinks, the temperature difference at the so-called "pitch point" can be raised by the gliding evaporation and condensation. This leads to improved heat transmission due to the higher driving average temperature difference.

Screw and scroll compressors can be adapted by construction as an expander for ORC systems. BITZER has been involved in various projects for several years and has already been able to gain important insights with this technology, which have been implemented in the design of screw expanders and their application. An individual expander design is available upon request.

A comprehensive description of ORC systems would go beyond the scope of this Refrigerant Report. Further information is available upon request.

09.20

Refrigerant	Type	Composition (with blends)	GWP AR4 (AR5)	Safety Group	Boiling temperature [°C]	Critical temperature [°C]
R1224yd(Z)	HCFO		4 (1)	A1	14.6	156
R1233zd(E)	HCFO		5 (1)	A1	18.3	166
R1336mzz(E)	HFO		– (7)	A1	7.6	130
R1336mzz(Z)	HFO		9 (2)	A1	33.5	171
R514A	HFO	R1336mzz(Z)/R1130(E)	7 (2)	A1	28.8	178

Tab. 6 Characteristics of HFO (HCFO) low-pressure refrigerants

Alternatives for R13B1

Besides R410A, ISCEON® MO89 (DuPont) can be regarded as potential R13B1 substitute. For R410A, a substantially higher discharge gas temperature than for R13B1 is to be considered, which restricts the application range even in 2-stage compression systems to a greater extent.

ISCEON® MO89 has been used for many years, preferably in freeze-drying plants. Meanwhile, production has ceased. However, for historical reasons the refrigerant will continue to be included in this Report. It is a mixture of R125 and R218 with a small proportion of R290. Due to the properties of the two main components, density and mass flow are relatively high, and discharge gas temperature is very low. Liquid subcooling is of particular advantage.

Both of the mentioned refrigerants have fairly high pressure levels and are therefore limited to 40..45°C condensing temperature with the usually applied 2-stage compressors. They also show less capacity than R13B1 at evaporating temperatures below -60°C.

In addition to this, the steep fall of pressure limits the application at very low temperatures and may require a change to a cascade system with e.g. R23, R508A/B or R170 (ethane) in the low temperature stage.

Lubrication and material compatibility are similar to other HFC blends.

The EU F-Gas Regulation (Annex III) provides an exemption "for applications designed to cool products below -50°C". This means that even after 2020, refrigerants with GWP > 2500 can be used in new plants. Due to the "phase-down" however, quantities will be limited, resulting in a considerable increase in price and very limited availability.

It is therefore imperative to develop alternative solutions for which, however, no overall recommendation is possible. Two-stage compressors may be operated e.g. with R448A/449A (safety group A1) or R1270 (A3) down to an evaporation temperature of -60..- 65°C. Although R404A/ R507A alternatives with GWP < approx. 250 (safety group A2L) are potentially possible, so far only limited experience has been gained even for typical low temperature refrigeration.

At evaporating temperatures of down to -50..-52°C, operation with CO_2 is also possible − either in a two-stage or a cascade system.

However, each variant generally requires a specific design and laboratory tests.

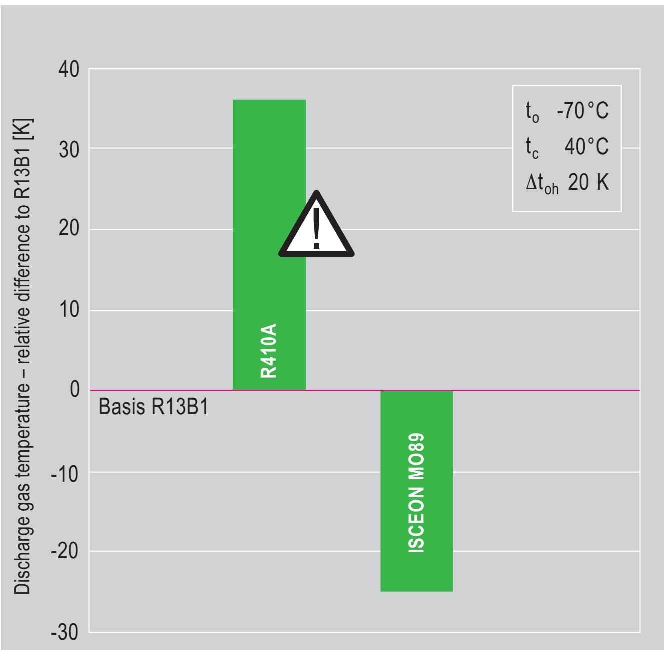


Fig. 33 R13B1/HFC alternatives – comparison of discharge gas temperatures of a 2-stage compressor

Alternatives for R13 and R503

For these substances, the situation is still quite favorable from a purely technical point of view; they can be replaced by R23 and R508A/R508B. R170 (ethane) is also suitable if the safety regulations allow a flammable substance (safety group A3).

Due to the partly steeper pressure curve of the alternative refrigerants and the higher discharge gas temperature of R23 compared to R13, differences in performance and application ranges for the compressors must be considered. Heat exchangers and controls have to be adapted individually.

As lubricants for R23 and R508A/B, polyol ester oils are suitable, but must be matched for the special requirements at extreme low temperatures.

R170 is also well soluble with conventional oils, but an adaptation to the temperature will be necessary.

Applications with these refrigerants are purely for cooling products below -50°C. Hence, the exemption described in the previous chapter in the EU F-Gas Regulation applies in particular.

For R23 and R508A/B, however, the effects of "phase-down" are particularly serious. The GWP values range from 13200 to 14800 (AR4). Even relatively small quantities are therefore very much at the expense of the available quotas.

Apart from R170 (ethane) with the special safety precautions required for A3 refrigerants, there are no directly comparable alternatives for R23 and R508A/B within the group of HFOs or HFO/HFC mixtures (safety groups A1 or A2L). In many cases, however, the use of A3 refrigerants is not possible or would involve unjustifiable expenses and high costs in the relevant special applications.

Following these challenges, the company Weiss Technik in cooperation with the TU Dresden has developed a non-flammable (A1) refrigerant mixture of R32, R125 and CO_2, which has proven to be a well suited alternative to R23, e.g. when used in so-called climatic stress chambers. It is marketed under the trade name WT69 and sold by TEGA Technische Gase. The refrigerant is now also listed in the ASHRAE nomenclature under R469A.

A major advantage over R23 is that the GWP is reduced by more than 90% (1398). This ensures at least medium to longer-term availability.

From a thermodynamic point of view, there are major differences to R23, therefore the suitability in the respective application must be checked individually. Although the differences in the boiling point are not large (-78.5°C vs. -82°C for R23), the mixture features a distinct temperature glide. Apart from the required specific design of the heat exchangers, this may affect the operating process and the compressor size.

Furthermore, research projects have been initiated that examine the use of N_2O (nitrous oxide) and mixtures of N_2O and CO_2 are examined in more detail. Extensive examinations and tests at the Karlsruhe University of Applied Sciences and the Institute of Air Handling and Refrigeration (ILK) in Dresden show revealing results.

N_2O (R744A) has similar thermodynamic properties and pressures as CO_2, identical molecular weight, a very low triple point (-90.8°C) and a critical temperature of 36.4°C. The GWP is 298, which is a fraction of the R23 and R508A/B values. In sum, an ideal alternative for special applications up to about -80°C evaporating temperature?

At first glance, these are very positive features. Unfortunately, there are also negative aspects that virtually preclude the use of N_2O as a pure substance.

Pure N_2O as a refrigerant is a safety risk: It has a narcotic effect and promotes fire. N_2O can oxidize other substances. In addition, under specific conditions (pressure, temperature or ignition source), exothermic decomposition reactions can occur, which fundamentally call into question the permanently safe operation of a refrigeration system with pure N_2O.

By adding CO_2 in higher percentages (over approx. 15%), the triple point is slightly shifted towards higher temperatures, but at the same time a positive effect ("phlegmatization") on oxidation and chemical decomposition is achieved. The safety risk is reduced significantly, and material compatibility is considerably improved. Nevertheless, there are special challenges i.a. for lubricants with a high resistance to oxidation which must also be suitable for the special requirements at low temperature conditions.

Investigations are ongoing. A final assessment is not yet possible, which is why no guidelines can currently be drawn up for the design and implementation of such systems.

BITZER has carried out investigations and also collected experiences with several of the substitutes mentioned. Performance data and instructions are available upon request. Due to the individual system technology for these special installations, consultation with BITZER is necessary.

Lubricants for compressors

Positive displacement compressors – as are predominantly used in commercial and industrial refrigeration, air conditioning and heat pump systems – are commonly oil-lubricated. Despite appropriate constructional measures and/or installation of an oil separator, a small amount of oil is pumped into the circuit together with the compressed gas flow. To stabilise the oil balance, suitable measures for continuous oil return must be taken. Oils that are soluble and miscible with the refrigerant are advantageous. The refrigerant dissolved in the oil significantly reduces the viscosity, improving oil fluidity and minimising the negative influence on heat transfer in heat exchangers.

In the past, so-called naphthenic mineral oils and synthetic alkylbenzenes were preferred. For systems with CFC and HCFC refrigerants (for example R22) and hydrocarbons, they are very favorable with regard to solubility and miscibility. On the other hand, owing to their low polarity, they are insufficiently miscible with the highly polar HFC and HFO refrigerants and are therefore not properly and sufficiently drawn into the refrigeration cycle.

Immiscible oils can accumulate in the heat exchangers and hinder the heat transfer so much that operation of the system is no longer possible.

Therefore, new lubricants with appropriate solubility/miscibility have been developed for systems with HFC and HFO refrigerants. These are oils based on polyol ester (POE) and polyalkylene glycol (PAG).

They have similar or better lubricating properties than previously customary oils, but are more or less hygroscopic, depending on the refrigerant solubility. This requires special care in manufacturing (including drying), transport, storage and charging, so that chemical reactions in the plant – such as hydrolysis in POE – are avoided.

PAG-based oils are particularly critical concerning water absorption. In addition, they have a relatively low dielectric strength and are therefore less suitable for semi-hermetic and hermetic compressors. They are primarily used in mobile air conditioning systems with open drive compressors, where special requirements for lubrication and best solubility/miscibility are required because of a high oil circulation rate. To avoid copper plating, non-ferrous metals are used in these systems.

The remaining refrigeration industry so far prefers POE oils. The extensive experience gained with them is positive if the water content in the oil does not significantly exceed 100 ppm. However, only oils specified by the compressor manufacturer may be used. Because of the increased reactivity of HFOs with oil, this is especially true for systems with these refrigerants.

Compressors for factory-made air conditioners and chillers are also increasingly being charged with polyvinyl ether (PVE) oils. Although they are more hygroscopic than POE, they are very resistant to hydrolysis, thermally and chemically stable, have good lubricating properties and high dielectric strength. In contrast to POE, they are less prone to the formation of metal soaps and thus offer more security against blockage of capillaries.

Special requirements for the lubricants exist with CO_2 systems. Specially formulated POEs are also suitable for use in widely ramified pipe networks due to their particularly good solubility/miscibility. However, these properties have a negative effect on viscosity and lubricity (tribology) and therefore require compressors with an extremely robust and wear-resistant drive gear. At very high loads, e.g. heat pumps, PAG oils specially developed for CO_2 applications ensure even more favorable lubrication conditions.

Due to the thermodynamic properties of ammonia (NH_3) and the resulting plant engineering, non-soluble/miscible oils are advantageous. These include for example mineral oils and polyalphaolefins (PAO). However, they require a special technique for oil separation and oil recirculation. For further explanation as well as additional information on applications when using partially soluble PAG oils see chapter NH_3 (Ammonia) as alternative refrigerant (page 28) and supplementary information (see below).

Further information see Fig. 37 “Overview lubricants”, page 45 and explanations for the particular refrigerants.

Supplementary BITZER information concerning lubricants (see also https://www.bitzer.de)

- ❏ **Technical Information KT-500 „BITZER refrigeration compressor oils for reciprocating compressors”**
- ❏ **Technical Information ST-500 „BITZER refrigeration compressor oils for screw compressors“**
- ❏ **Technical Information EST-500 „BITZER refrigeration compressor oils for scroll compressors – stationary applications"**
- ❏ **Technical Information AT-640 „Use of ammonia (R717) in BITZER compressors” – chapter: "Oils and their influence on the system design"**
- ❏ **Technical Information AT-660 „Use of propane (R290) and propene (R1270) in semi-hermetic BITZER compressors” – chapter: "Oils“**
- ❏ **Operating Instructions KB-120 and KB-130 „Semi-hermetic reciprocating compressors for CO_2 applications“**

Refrigerant type	Composition (Formula)	Substitute / Alternative for	Application range	ODP [R11=1.0]	GWP$_{(100a)}$ ⑤⑥ [CO_2=1.0] AR4 (AR5)	Safety group ④	Practical limit [kg/m³] ⑤
HCFC-Refrigerants							
R22	$CHClF_2$	R502 (R12①)		0.055	1810 (1760)	A1	0.3
R124	$CHClFCF_3$	R114①, R12B1		0.022	609 (527)	A1	0.11
R142b	$CClF_2CH_3$			0.065	2310 (1980)	A2	0.049
HFC Single-component Refrigerants							
R134a	CF_3CH_2F	R12 (R22①)	see page 44	0	1430 (1300)	A1	0.25
R152a	CHF_2CH_3	mainly used as part components for blends			124 (138)	A2	0.027
R125	CF_3CHF_2				3500 (3170)	A1	0.39
R143a	CF_3CH_3				4470 (4800)	A2L	0.048
R32	CH_2F_2	R410A (R22)			675 (677)	A2L	0.061
R227ea	CF_3-CHF-CF_3	R12B1, R114①			3220 (3350)	A1	0.63
R236fa	CF_3-CH_2-CF_3	R114			9810 (8060)	A1	0.59
R23	CHF_3	R13 (R503)			14800 (12400)	A1	0.68
HFC Blends							
R404A	R143a/125/134a	R22 (R502)	see page 44	0	3922 (3940)	A1	0.52
R507A	R143a/125				3985 (3990)	A1	0.53
R407A	R32/125/134a				2107 (1920)	A1	0.33
R407F	R32/125/134a				1825 (1670)	A1	0.32
R407H	R32/125/134a				1490 (1380)	A1	0.38
R422A	R125/134a/600a				3143 (2850)	A1	0.29
R437A	R125/134a/600/601	R12 (R500)			1805 (1640)	A1	0.081
R407C	R32/125/134a	R22			1774 (1620)	A1	0.31
R417A	R125/134a/600				2346 (2130)	A1	0.15
R417B	R125/134a/600				2920 (2740)	A1	0.069
R422D	R125/134a/600a				2729 (2470)	A1	0.26
R427A	R32/125/143a/134a				2138 (2020)	A1	0.29
R438A	R32/125/134a/600/601a				2264 (2060)	A1	0.079
R410A	R32/125	R22① (R13B1②)			2088 (1920)	A1	0.44
R508A	R23/116	R503			13210 (11600)	A1	0.23
R508B	R23/116				13400 (11700)	A1	0.25
HFOs and HFO/HFC Blends – further blends and data see pages 24 to 27							
R1234yf	$CF_3CF=CH_2$	R134a	see page 44	0	4 (< 1)	A2L	0.058
R1234ze(E)	$CF_3CH=CHF$				7 (< 1)	A2L	0.061
R513A (XP10)	R1234yf/134a				631 (573)	A1	0.35
R450A (N-13)	R1234ze(E)/134a				605 (547)	A1	0.319
R471A	R1234ze(E)/1336mzz(E)/227ea	R134a①			148 (148)	A1	N/A
R515B	R1234ze(E)/227ea				293 (299)	A1	0.29
R448A (N-40)	R32/125/1234yf/1234ze(E)/134a	R404A, R507A			1387 (1270)	A1	0.388
R449A (XP40)	R32/125/1234yf/134a				1397 (1280)	A1	0.357
R454C	R32/1234yf				148 (146)	A2L	0.059
R455A	R32/1234yf/CO_2				148 (146)	A2L	0.105
R452B	R32/125/1234yf	R410A			698 (676)	A2L	0.062
R454B	R32/1234yf				466 (467)	A2L	0.061
Halogen free Refrigerants							
R717 (NH_3)	NH_3	R404A (R22)	see page 44	0	0	B2L	0.00035
R723	NH_3/R-E170	R404A (R22)			1	B2	N/A
R600a	C_4H_{10}	R134a①			3	A3	0.011
R290	C_3H_8	R404A (R22)			3	A3	0.008
R1270	C_3H_6	R404A (R22)			2	A3	0.008
R170	C_2H_6	R23			6	A3	0.008
R744 (CO_2)	CO_2	Diverse			1	A1	0.07

Tab. 7 Refrigerant properties (continued on Tab. 8)

These data are valid subject to reservations; they are based on information published by various refrigerant manufacturers.

① Alternative refrigerant has larger deviation in refrigerating capacity and pressure

② Alternative refrigerant has larger deviation below -60°C evaporating temperature

③ Also used as a component in R290/600a-Blends (direct alternative to R12)

④ Classification according to EN 378-1 and ASHRAE 34

⑤ According to EN 378:2016

⑥ AR4: according to IPCC IV – time horizon 100 years – also basis for EU F-Gas Regulation 517/2014
AR5: according to IPCC V – time horizon 100 years

N/A Data not yet published.

Refrigerant type	Boiling temperature [°C] ①	Temperature glide [K] ②	Critical temperature [°C] ①	Cond. temp. at 26 bar (abs) [°C] ①	Refr. capacity [%] ③	Discharge gas temp. [K] ③	Lubricant (compressor)
HCFC-Refrigerants							
R22	-41	0	96	63	80 (L) ④	+35 ④	
R124	-12	0	122	105	⑤	⑤	
R142b	-9	0	137	112			
HFC Single-component Refrigerants							
R134a	-26	0	101	79	97 (M)	-8	
R152a	-24	0	113	85			
R125	-49	0	66	51	⑤	⑤	
R143a	-47	0	73	55			
R32	-52	0	78	42	108 (H)	+21	
R227ea	-16	0	102	96	⑤	⑤	
R236fa	-2	0	125	115			
R23	-82	0	26	2	⑤	⑤	
HFC Blends							
R404A	-46	0.7	72	56	105 (M)	-34	
R507A	-47	0	71	54	107 (M)	-34	
R407A	-45	6.5	82	59	98 (M)	-19	
R407F	-46	6.4	83	57	104 (M)	-11	
R407H	-45	7.0	87	60	99 (M)	-8	
R422A	-47	2.5	71	55	100 (M)	-39	
R437A	-32	3.5	95	75	108 (M)	-7	
R407C	-44	7.1	86	61	100 (H)	-8	
R417A	-39	5.0	85	67	97 (H)	-25	
R417B	-45	3.4	74	58	95 (M)	-37	
R422D	-43	4.9	78	62	90 (M)	-36	
R427A	-43	6.8	85	63	90 (M)	-20	
R438A	-42	6.2	83	64	88 (M)	-27	see page 45
R410A	-51	0	71	43	140 (H)	-4	
R508A	-88	0	10	-3	⑤	⑤	
R508B	-88	0	11	-3			
HFO and HFO/HFC Blends – further blends and data see pages 24 to 27							
R1234yf	-30	0	95	82	98 (M)	-14	
R1234ze(E)	-19	0	109	92	75 (H)	-6	
R513A (XP10)	-30	0	95	78	102 (M)	-7	
R450A (N-13)	-23	0.6	104	86	88 (M)	-6	
R471A	-17	3.2	112	97	67 (H)	-7	
R515B	-19	0	109	93	75 (H)	-7	
R448A (N-40)	-46	6.2	83	58	96 (M)	+12	
R449A (XP40)	-46	5.7	82	58	96 (M)	+12	
R454C	-46	7.8	86	64	86 (M)	+7	
R455A	-52	12.9	86	61	93 (M)	+10	
R452B	-51	0.9	77	46	98 (H)	+7	
R454B	-51	1.0	78	47	97 (H)	0	
Halogen free Refrigerants							
R717 (NH_3)	-33	0	132	60	100 (M)	+60	
R723	-37	0	131	58	105 (M)	+35	
R600a	-12	0	135	115	55 (H)	-9	
R290	-42	0	97	70	86 (M)	+4	
R1270	-48	0	91	61	104 (M)	+12	
R170	-89	0	32	4	⑤	⑤	
R744 (CO_2)	-57 ⑥	0	31	-11	⑤	⑤	

Tab. 8 Refrigerant properties

① Rounded values

② Total glide from bubble to dew line – based on 1,013 bar (abs.) pressure. Real glide dependent on operating conditions. Approx. values in evaporator: H/M 70%; L 60% of total glide

③ Reference refrigerant for these values is stated in Tab. 7 under the nomination "Substitute for" (column 3) Letter within brackets indicates operating conditions
H High temp (+5/50°C)
M Medium temp (-10/45°C)
L Low temp (-35/40°C)

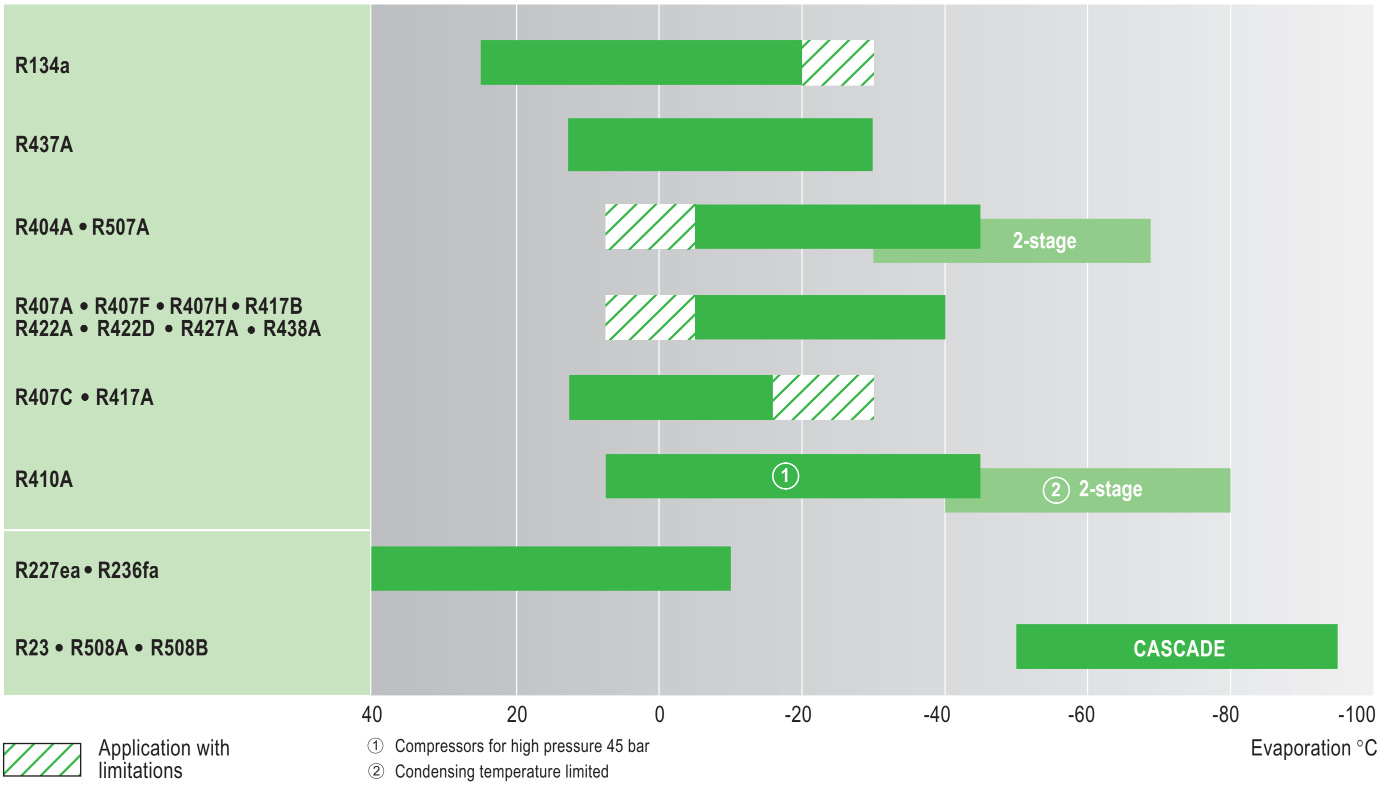
④ Valid for single stage compressors

⑤ Data upon request (operating conditions must be given)

⑥ Triple point at 5.27 bar

Stated performance data are average values based on calorimeter tests.

HFC refrigerants

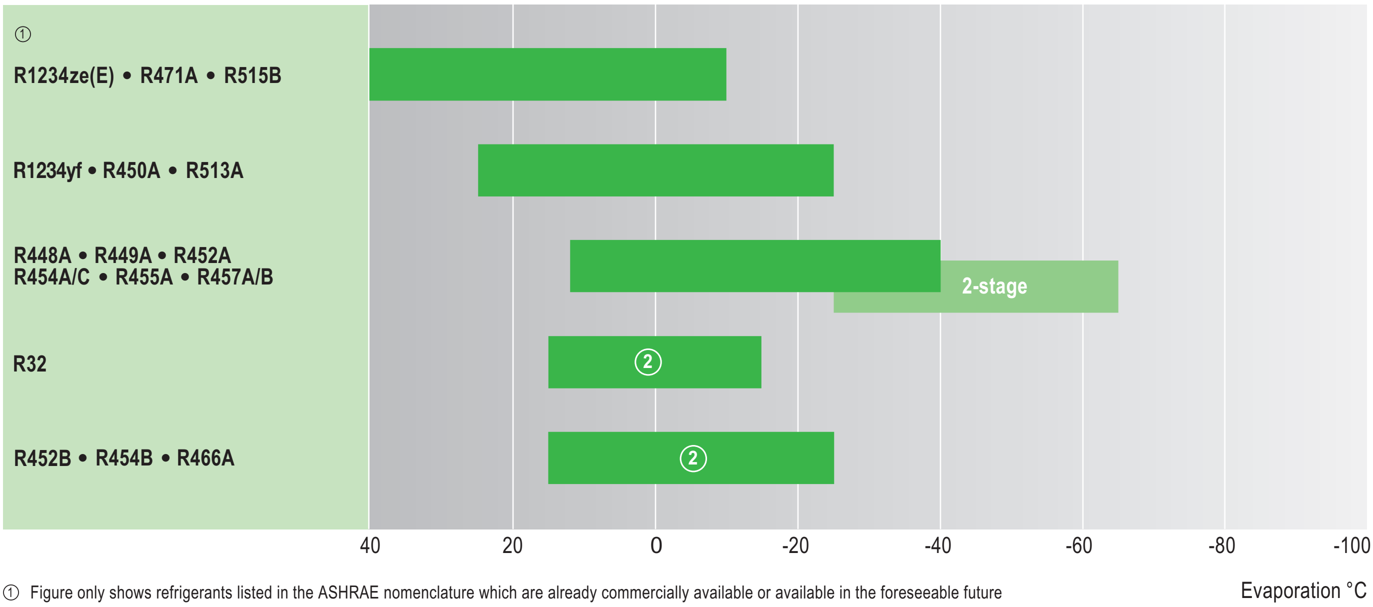


Application with limitations

① Compressors for high pressure 45 bar
② Condensing temperature limited

Fig. 34 Application ranges for HFC refrigerants (ODP = O)

"Low GWP" refrigerants (HFO, HFO/HFC blends, R32)



① Figure only shows refrigerants listed in the ASHRAE nomenclature which are already commercially available or available in the foreseeable future
② Compressors for high pressure 45 bar

Fig. 35 Application ranges for "Low GWP" refrigerants (HFO, HFO/HFC blends, R32)

Halogen free refrigerants

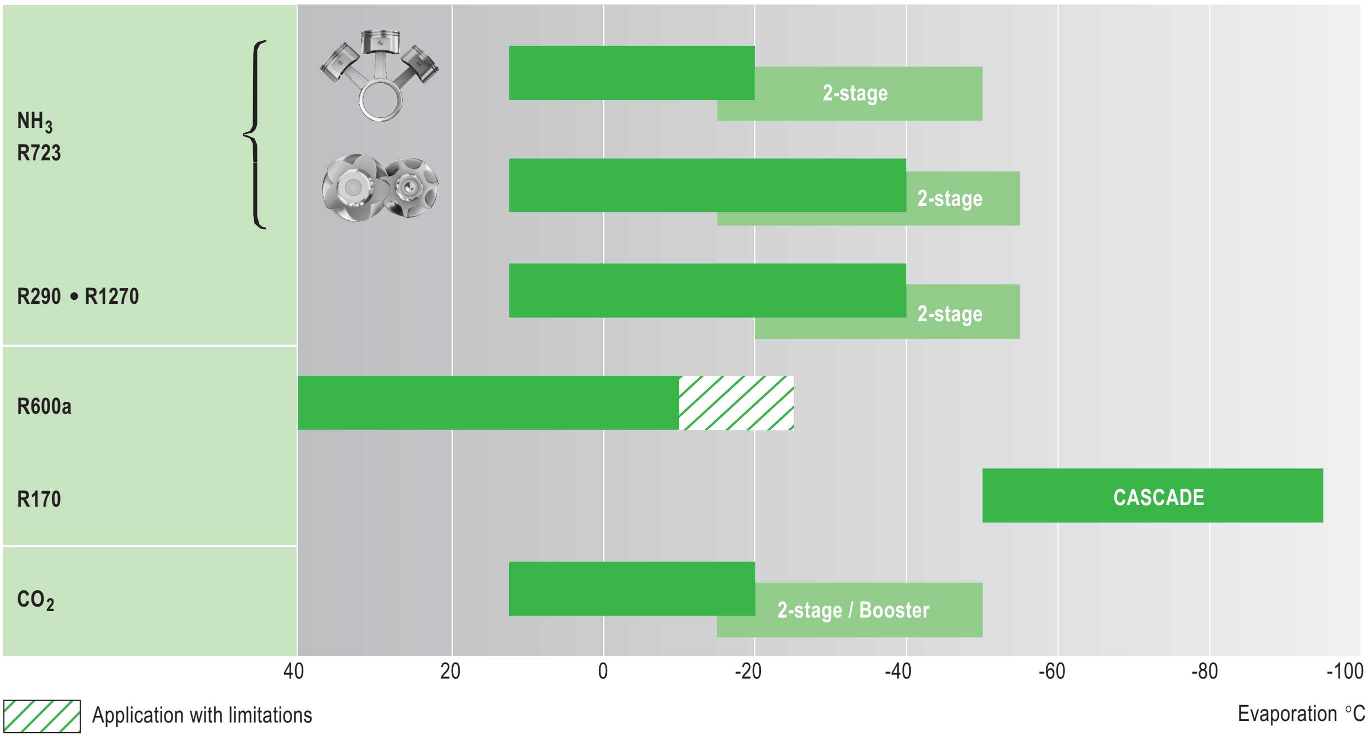


Fig. 36 Application ranges for halogen free refrigerants

Overview lubricants

	Traditional oils				New lubricants			
	Mineral oil (MO)	Alkyl-benzene (AB)	Mineral oil +alkyl-benzene	Poly-alpha-olefin (PAO)	Polyol ester (POE)	Polyvinyl-ether (PVE)	Poly-glycol (PAG)	Hydro cracked mineral oil
(H)CFC	Good suitability	Good suitability	Good suitability	Application with limitations	Application with limitations, ⚠ +VG	Not suitable	Not suitable	Not suitable
Service blends with R22	Application with limitations	Good suitability	Good suitability	Not suitable	Good suitability, ⚠ +VG	Not suitable	Not suitable	Not suitable
HFC + blends	Not suitable	Application with limitations	Not suitable	Not suitable	Good suitability	Good suitability	Application with limitations, ⚠	Not suitable
HFC/HC blends	Suitability dependant on system design	Suitability dependant on system design	Suitability dependant on system design	Not suitable	Good suitability	Good suitability	Not suitable	Not suitable
HFO+HFO/HFC blends	Not suitable	Not suitable	Not suitable	Not suitable	Good suitability, AD	Good suitability, AD	Not suitable	Not suitable
Hydrocarbons	Good suitability, VG	Application with limitations, VG	Application with limitations, VG	Good suitability, VG	Good suitability, VG	Not suitable	Application with limitations, ⚠	Not suitable
NH_3 • R723	Good suitability	Application with limitations	Application with limitations	Good suitability	Not suitable	Not suitable	Application with limitations, ⚠	Good suitability
CO_2	Not suitable	Not suitable	Not suitable	Suitability dependant on system design	Good suitability, AD	Not suitable	Good suitability, AD	Not suitable

Good suitability
Application with limitations
Suitability dependant on system design
Not suitable
⚠ Especially critical with moisture
VG Possible higher basic viscosity
AD Possible specia formulation

Further information see chapter Lubricants for compressors (page 41) and explanations for the particular refrigerants

Fig. 37 Lubricants for compressors

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